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FELLMONGERS HANDBOOK

By

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PREFACE

The fellmongering industry in New Zealand operates under conditions quite different from those in other parts of the world. Anyone overseas who should happen to read this book may be interested to know what these conditions are.

Approximately 19 million sheep and lamb skins are produced in New Zealand each year, and of these, the overwhelming majority are processed in fellmongeries which form an integral part of the freezing works (our American friends would call them "packing plants") where the stock is killed. A small freezing works would handle 3,000 animals per day, while a large one would handle over 15,000 per day at the peak of the season and perhaps two-thirds of that number on an average over the rest of the season. The season lasts for approximately seven months of the year, of which six to eight weeks could be described as "peak", although the duration of the season and especially of the peak varies considerably in different parts of the country and from year to year. This scale of operations has brought its own peculiar problems and has given rise to its own techniques.

The skins have to be handled quickly as they come from the slaughter board and, except for keeping sheep and lambs separate, any system of sorting them into grades prior to processing is quite out of the question. A "dolly" or paddle in which the pelts are processed may hold anything from 600 to 2,000 pelts, which may be a mixture of types, and all of which must perforce be given identical treatment. At the end of the allotted time, the pelts must come out to make room for the next batch. To provide extra equipment to allow for delays would obviously be uneconomic, and there is never any question of stopping killing because of a hold-up in the fellmongery. The skins are coming to the fellmongery steadily, usually by conveyor or water flume and, as fast as they come, they must be disposed of.

The employment is seasonal, and the fellmongery hands, like those in the rest of the freezing works, change frequently. There is no possibility of building up a permanent, skilled labour force. Only the fellmonger and his senior assistants are permanently employed.

Very few pelts are tanned locally. They are almost all exported in the pickled condition, mainly to the United States. The fellmonger has no idea at all as to what type of leather his pelts will be used for, but he does know that they sometimes lie in casks for anything up to two years in the overseas tanners' yards.

The fellmonger, in coping with his technical problems, is handicapped by the fact that there are in New Zealand no technical schools offering courses designed to suit his needs. He has to "pick up" his knowledge as best he can, aided in no small measure by the circulars issued by the New Zealand Leather and Shoe Research Association and by the papers presented at the Annual Conference organised by the Association. What he remembers of his school chemistry is usually woefully inadequate, and this situation is liable to worsen with the tendency for "general science" to replace "chemistry" and "physics" in the school syllabus. The only available books dealing with fellmongering in any way are written for tanners or leather chemists, and are completely unsuitable for the New Zealand fellmonger.

This book, then, is an attempt to present in a readily accessible and, it is hoped, a readily assimilable form, the fundamental principles on which the practice of fellmongery is based. It assumes no knowledge of chemistry on the part of the reader, but it does assume a familiarity with the practical side of fellmongering and of its technical terms. It assumes, for instance, that the reader has handled the various chemicals used in the fellmongery and knows their common names, at least. It also assumes that he has carried out titrations for the control of lime and pickle liquors.

It will be noticed that only very rarely have definite concentrations of materials been specified or definite directions given. This has been deliberate. Raw materials, climatic conditions, and layout of plant vary so much from one fellmongery to another that any attempt to be specific would be doomed to failure. If this book can give the fellmonger a foundation on which to build up his practical experience, it will have achieved its purpose.

The material which is presented here has been drawn from many sources. Most of it has come from circulars and conference reports issued by the New Zealand Leather and Shoe Research Association, but *Fellmongery Investigations* and other publications of the CSIRO, Australia, as well as such books as *The Chemistry of Leather Manufacture* by McLaughlin and Theis, *Fundamentals of Leather Science* by Woodroffe, and *Progress in Leather Science* published by the BLMRA have been consulted freely.

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Chapter 1

THE STRUCTURE OF THE SHEEPSKIN

In the study of any manufacturing process the starting point must obviously be the raw material used, since its nature and composition determine the treatment required to produce the desired finished product. In this study of the fellmongering processes we shall therefore start with a description of the sheepskin itself.

The account given here is not by any means a full and exhaustive description of the structure and nature of the sheepskin. We shall confine ourselves to those features which have a bearing on the working of the pelts and which are therefore of practical interest to the fellmonger. Also we shall leave until Chapter 2 an account of the chemical nature of the various constituents of the skin.

The structure of the skin with which we are concerned is its arrangement in layers from the grain side down to the flesh side. To see this arrangement, we have to cut a cross section of the skin and then, since the detail is too fine to be seen with the naked eye, we have to look at it through a microscope. Plate 1 is a photograph of a typical cross section of a sheepskin as it appears when viewed through a microscope. It is magnified about 60 times. A photograph taken through a microscope in this way is called a *photomicrograph*. It is rather difficult at first to pick out in an actual photograph the essential features of the skin, although this becomes easier with practice. To help you get your bearings, so to speak, we have drawn fig. 1, which is a key to plate 1. In fig. 1 the most important features have been emphasised and labelled, while the unimportant details have been omitted altogether. If you care to spend a little time studying plate 1 and fig. 1, you should soon be able to pick out the essential features of a skin on any photomicrograph.

The sheepskin resembles that of most other animals in that, as will be seen, it consists of two main layers – a very thin outer layer called the *epidermis* and a much thicker inner layer called the *dermis* or true skin. It is only the dermis which is converted into the finished pelt and finally into leather, but the fellmonger has to deal with the epidermis as well. It will therefore pay us to look at each of these layers a little more closely.

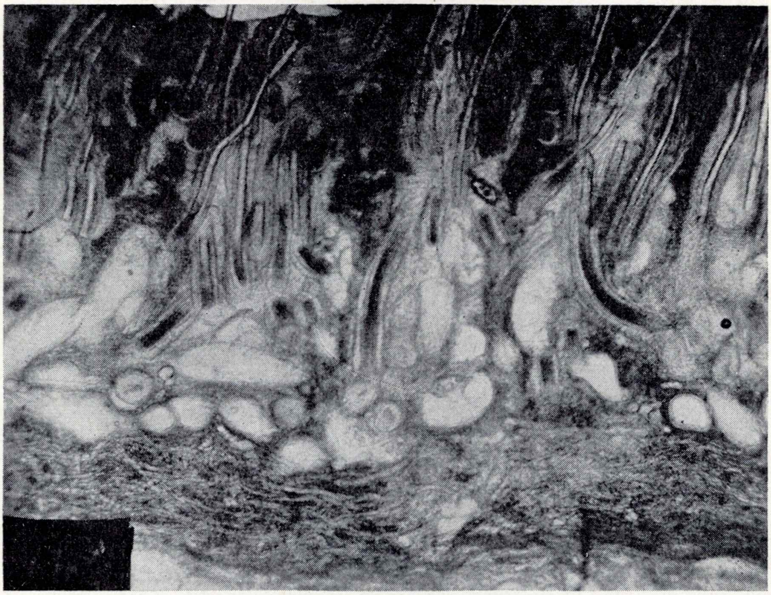


PLATE 1. Photomicrograph of typical skin section

THE EPIDERMIS

The epidermis, although shown in fig. 1 as a single layer, is really a complex structure, consisting in itself of several layers, but since it is removed entirely during the fellmongering processes, these details are of little interest to the fellmonger. It should be mentioned, however, that the chemical composition of the epidermis is rather like that of wool, and is very different from that of the dermis or true skin. Depilatory paint therefore attacks the epidermis in much the same way as it does wool. You will see from fig. 1 that the epidermis, as well as forming a protective outer coating over the true skin, also lines the deep pockets in which the wool follicles lie, and acts as a sheath around the follicles and wool roots. When the depilatory paint penetrates through from the flesh side, it attacks this sheath as well as the wool root itself, and thus loosens the wool follicle in its pocket. At times, and especially when the paint is on the strong side, portions of the epidermis are loosened by the action of the paint and come away attached to the wool as what the New Zealand fellmonger calls "scud". This is, of course, undesirable, and the epidermis should remain on the pelt until it is disintegrated by the action of the lime liquor.

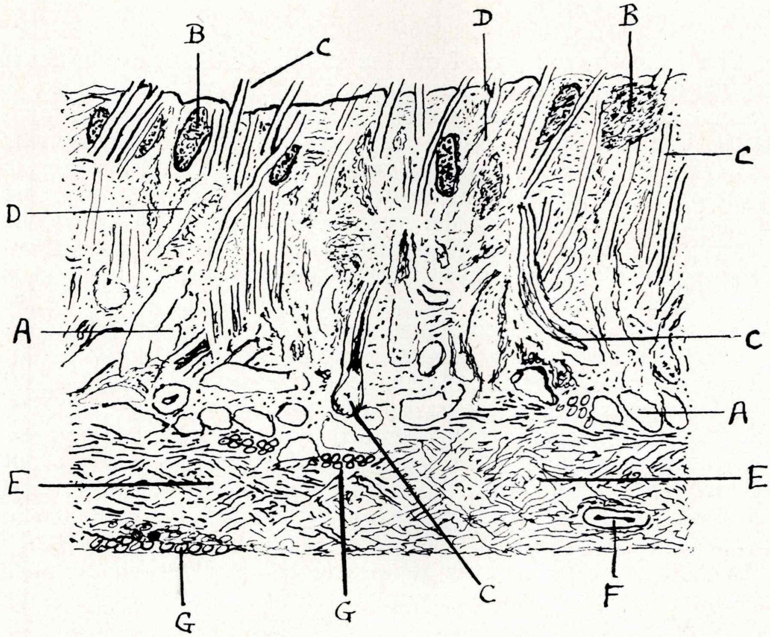


FIG. 1. Diagram of plate 1: (A) sweat glands; (B) fat glands; (C) wool fibres and roots; (D) erector pili muscles; (E) corium fibres; (F) blood vessel; (G) fat cells.

THE DERMIS

The dermis or true skin is the portion of the sheepskin which, after treatment by the fellmonger, becomes the pelt of commerce. It is necessary, therefore, to give it rather more attention than we gave the epidermis. Again, fig. 1 will give us a clearer picture of the structure than will plate 1, although you should study that too, and try to become familiar with the various features as they appear in photographs. As you examine photomicrographs of other skins you will find wide variations from the structures shown in fig. 1 and in plate 1, but all skins, although they may differ considerably in detail, do conform to the same general pattern. The dermis is divided into two main layers, the grain layer or *thermostat layer* and the flesh layer or *corium*. We shall deal with each of them in turn.

Grain Layer

The grain layer extends from the surface of the true skin down to roughly the base of the wool roots. Like the flesh layer, it consists mainly of fibrous tissue, but unlike the flesh layer, it contains large numbers of other structures such as, for instance, the wool follicles, the sweat glands, and the fat glands. These organs are the ones concerned with regulating the body temperature, and it is for this reason that the grain layer is often known as the "thermostat layer". In hot weather the sweat glands, or "sudoriferous glands" as the scientist with his fondness for big words calls them, secrete perspiration whose evaporation on the surface of the skin cools it down. In cold weather the fat glands or "sebaceous glands" secrete an oily substance which retards evaporation of moisture from the skin and thus helps to keep the animal warm. This oily substance is the main constituent of wool grease. The fat glands, by the way, are controlled by tiny muscles, the *erector pili* muscles, which in cold weather contract and squeeze oil out of the glands. At the same time these muscles force the wool fibres to stand more erect and produce a "goose-flesh" appearance in the skin.

Although the grain layer appears to be mainly taken up with structures such as wool fibres and glands, it does contain a large amount of fibrous tissue consisting almost entirely of a protein called *collagen*. Collagen is one of those proteins like wool and silk which occur in long, relatively strong threads or fibres. We shall have much more to say in Chapter 2 about the nature and chemical properties of proteins in general and of collagen in particular, but at this point we must have a look at the structure of the collagen fibres as they occur in the sheepskin, because this structure is of the utmost importance from the fellmonger's point of view.

In recent years the invention of a new scientific instrument has made it possible to obtain a great deal more information about the structure of collagen fibres than we ever had before. This new instrument is the electron microscope. There is no need for us to bother about how the electron microscope works. It is much more complicated and much more expensive than the ordinary microscope and it requires a specially trained operator to use it. But whereas an ordinary microscope can magnify things up to about 1,500 times, an electron microscope can magnify more than 50,000 times, and can thus reveal very much more detail in microscopic objects. We have such instruments in this country, and electron-photomicrographs of New Zealand pelts have been taken.

The electron microscope has shown that the basic structural unit of collagen in the skin is what is known as the *unit fibril*. The unit fibrils are long, cylindrical threads of collagen, having a uniform diameter throughout their length and all having the same diameter. Typical unit fibrils from sheepskin are shown magnified 55,000 times in plate 2. Do not take any notice of the alternating light and dark bands on these fibrils. They are of great interest to the protein chemist but do not directly concern the fellmonger or the tanner.

The unit fibrils do not occur singly in a sheepskin, but are twisted together to form fibres in much the same way as the separate strands are twisted together to form a rope. Not only are the fibrils twisted, but they are also cemented together with protein matter which, in the older books, was called *reticulin*. Doubt is now cast on the existence of reticulin in the skin, and it is thought that the cementing substance is *procollagen* (a primitive or immature form of collagen) or else collagen itself. But whatever its nature, it serves to bind the unit fibrils together and, as well, forms sheaths and "garters" round the fibres. The fibres, therefore, unlike ropes, do not depend entirely for their strength and cohesion on the twisting together of the unit fibrils. The fibres can contain up to about 25 unit fibrils and can therefore vary greatly in thickness according to their position and function in the skin. Plate 3 shows how the fibres are built up out of unit fibrils, which are enclosed in a sheath of collagen which isolates the fibre bundles from one another.

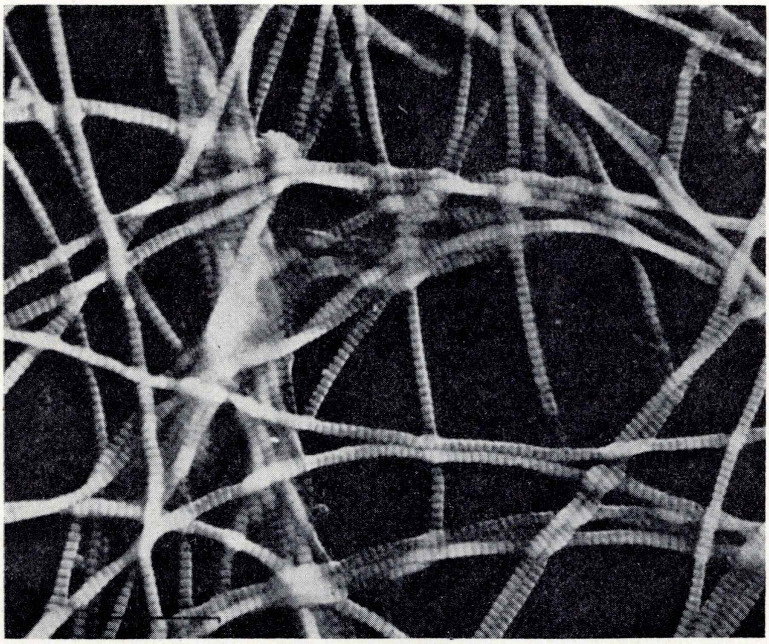


PLATE 2. Electron photomicrograph of unit fibrils

Then the fibres themselves are in most cases twisted together and held by *protein* fibres to give thicker and stronger structures which we may call *fibre bundles*. The fibre bundles and the thicker fibres are big enough to show in an ordinary photomicrograph, and you can see what they look like in plate 4.

The unit fibrils, although they are the basic units of the skin, can in fact be broken down into still finer collagen threads called *filaments*. This is illustrated in plate 5. It takes fairly severe treatment, such as the action of bacteria or of strong acids or alkalis, to break a unit fibril into its filaments and, once this has been done, all the valuable properties of the collagen fibre disappear. A filamented unit fibril has no mechanical strength and little resistance to chemical attack. It is mainly the characteristics of the collagen fibres which make leather such a valuable material for so many different purposes, and these characteristics depend absolutely on the unit fibrils being kept intact throughout all the various processes of fellmongering and tanning. Every unit fibril which has become filamented is so much valuable raw material lost. It is for this reason that we said that the unit fibril and not the filament was the basic structural unit of collagen in the skin. There are advantages if, in the working of the pelt, the fibre bundles are separated into their component fibres and the fibres

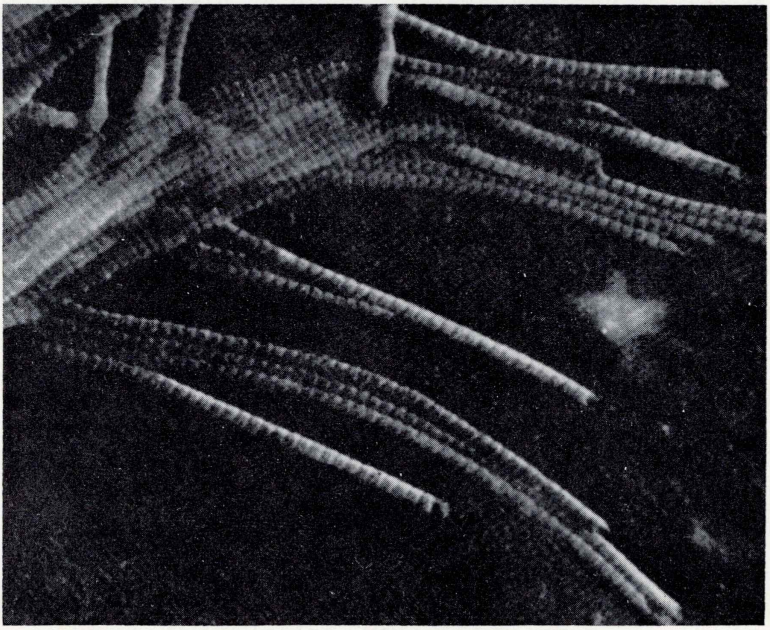


PLATE 3. Electron photomicrograph of fibres

into their individual unit fibrils, but there is the gravest disadvantage if the unit fibrils are broken down into filaments. Filamentation can produce only weakness and damage to the pelt, and is to be avoided at all cost.

Apart from the structures we have already mentioned, the grain layer contains numerous blood vessels, nerves, and fat cells, but, with the exception of the fat cells, these are usually not very prominent. In both the grain layer and the flesh layer there are present fibrous proteins and other more or less soluble substances which are necessary for the nourishment and growth of the skin and wool, and which must be removed during the fellmongering process, so that subsequently the tan liquors can readily penetrate the pelt and act on the collagen fibres. In the skin the fibres and fibre bundles are surrounded by a soft mucous substance, often called the *interfibrillary tissue.* When a sheepskin is dried, this interfibrillary tissue becomes hard and cement-like, thus giving the dried skin a parchment-like appearance and causing it to be hard and tinny. Together with the other non-fibrous substances, the interfibrillary tissue is removed during fellmongering. None of this non-fibrous matter shows up clearly in a photomicrograph, but it obscures the detail of the fibrous structure by making the photograph hazy.

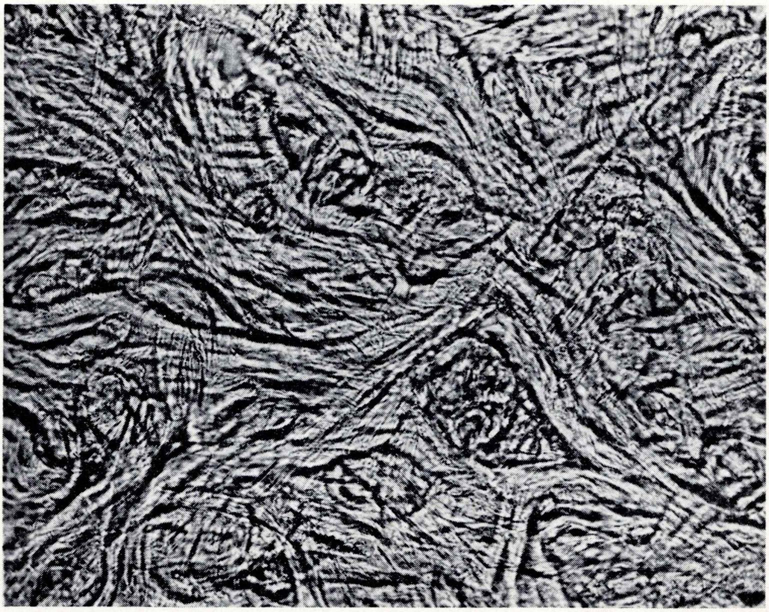


PLATE 4. Ordinary photomicrograph of fibres and fibre bundles

Junction of Grain and Flesh Layers

In most skins there is a well marked boundary between the grain layer and the flesh layer. You can see it quite clearly in plate 1. This boundary marks a plane of weakness in the skin which persists right through the fellmongering and tanning processes. The grain layer is not particularly strongly attached to the flesh layer and the attachment is not uniform over the whole area of the skin; there is a sort of network of lines of strong attachment with the areas inside the meshes much more loosely attached. The effect is something like that of a quilted material where the two outer layers are attached by rows of parallel stitching in two directions at right angles, leaving squares all over it where the layers are not attached at all. In a sheepskin the loosely attached areas are irregular both in size and shape, but the lines of strong attachment are usually about 1 or 2 in. apart.

Flesh Layer

The flesh layer or *corium* consists almost entirely of collagen fibres and is practically free from other structures except for some blood vessels and nerves. The fibres are, however, set in interfibrillary tissue, and nutrient substances are present in the same manner as in the grain layer. In the flesh layer the fibres tend to be thicker and more closely interwoven than in the grain layer,

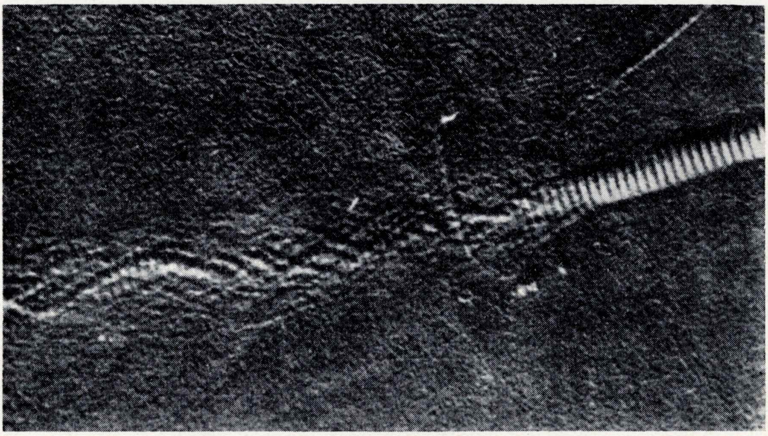


PLATE 5. Electron photomicrograph of filamented unit fibril

(Plates 2, 3, and 5 taken from
Burton, D., and Reed, R.,
J. Soc. Leather Trades Chem.
37: 13–22, 1953.)

and the weave is less interrupted by the presence of other structures. The fibres have a wave-like form, those running in one direction fitting into the depressions in the waves of those running more or less at right angles. The fibres tend to form layers lying at an angle to the surface of the skin, but the angle is less in the skin of the sheep than in most other animals. In the sheepskin the weave runs almost parallel to the surface of the skin, and the sheepskin is therefore said to have a "low angle of weave".

As was mentioned above, the collagen fibres consist of numerous unit fibrils held together partly by the twisting of the fibrils and partly by the cementing substances which are of a protein nature. During liming the chemical action of the alkali dissolves these cementing substances to a certain extent and partly frees the unit fibrils from each other within the fibre. The outlines of the unit fibrils then become visible under the microscope. This phenomenon is known as *splitting,* and shows up in photomicrographs as striations extending along the length of the fibre. Although internally split, the fibre remains as one unit. When in the lime dolly, the fibre bundles are swollen and tender, with the result that any mechanical action will cause them to tear apart. Paddling during liming will therefore tend to open up the fibre bundles and to break them down into smaller bundles. This is known as *separation.* A moderate degree of both separation and splitting is desirable in a pelt, in order that the tan liquors may be able to penetrate the fibre structure completely, but the opening up must not be too drastic. You should keep clearly in mind the distinction between separation and splitting. Separation is the breaking down of the fibre bundles into smaller ones, and is caused mainly by the mechanical action of the paddles in the lime dolly. Splitting is the division of the fibres into unit fibrils and is caused by the chemical action of the alkali in the lime liquor.

In both the grain layer and the flesh layer, fat cells are distributed in a manner which varies widely from skin to skin. In some cases there is hardly any fat at all, while in others there are so many fat cells that the fibrous structure is very thin and weak. It is quite common to find the fat cells arranged in chains either alongside the wool follicles or in parallel layers near the junction of the grain and flesh layers. In fact, this last arrangement is so common that some books state that the dermis is divided into three layers – the grain layer, the flesh layer, and the fatty layer between them. It is strange that the amount of fat in the skin seems to have little relationship to the amount of fat in the carcase.

It has already been mentioned that individual variations from skin to skin are almost endless. Obviously, any attempt to give a comprehensive account of them is out of the question. There are, however, one or two general trends which are worth a little consideration, since they have quite an effect on the working of the skins.

VARIATIONS DUE TO BREED

Sheepskins can be classified broadly into fine-woolled skins, such as Merino or Southdown, and coarse-woolled, such as Lincoln or Leicester. We shall describe the main features of these two types. Cross-breds, which form the bulk of New Zealand's sheep population, are intermediate in character but generally tend towards one or other of the pure-bred types, although, of course, they show the characteristic features to a less marked degree. Differences between the two types are seen more clearly in the pure-breds.

Fine-woolled Skins

The pelt of a fine-woolled sheep such as the Southdown is thinner than that of a coarse-woolled sheep and tends to be somewhat spongy. In the extreme case of the Merino, the pelt is so thin and ribby that it is of very little commercial value. In the fine-woolled skin, the wool follicles, as would be expected, are very close together, because the animal needs more wool fibres per square inch to cover it than does a coarse-woolled sheep. The wool follicles are almost vertical, and are quite markedly curved.

In the fine-woolled skin, not only are the wool fibres more numerous and more closely spaced, but they also have a tendency to grow in groups or clumps of three or four fibres. The fibres in each clump are so close together as to be almost touching, and there is only a very thin partition of skin between them. Now, as we have seen already, there is a fairly deep pocket in the skin around each wool follicle, and this pocket remains as a minute hole or pore in the pelt when the wool fibre and its sheath of epidermis is removed by pulling, liming, and bating. In the case of the coarse-woolled skin these pores are arranged individually and are relatively widely spaced. Except under a magnifying glass, they are practically invisible. But with a fine-woolled skin the case is very different. In the first place, only a thin partition of skin separates the wool follicles in each clump, and it is very common for this thin partition to be torn out with the wool fibres during pulling. In this case the whole clump of three or four fibres together with the partitions between them come away as one piece, leaving a hole of perhaps 20 times the area of the pore in a coarse-woolled skin. In addition to this, it is commonly found that the whole clump is growing in a depression in the skin. In other words, the partitions between the individual fibres do not come up to the general level of the skin. Even if the partitions are left intact during pulling, they do not show on the surface of the pelt, and the general appearance is of a hole as large as the whole clump of wool fibres. Plate 6 shows both these cases admirably. In some instances the partitions have obviously been torn out during pulling, and in others they are still intact but are so far below the general skin surface as to be almost invisible. It is this characteristic of fine-woolled skins which gives rise to the *pinhole* pelts which they invariably produce. The problem of pinhole is thus one for the breeder and not for the fellmonger. It would appear that in recent years the incidence of pinhole has increased to a very marked extent in New Zealand, and that breeders, perhaps in an endeavour to remedy the "hairiness" which tended to appear in the coarser wools, have introduced finer-woolled strains with pinhole characteristics. Whether it is possible to produce a strain of sheep with wool which is free from hairiness and which, at the same time, grows in individual fibres instead of in clumps is a question which only breeders can answer.

Coarse-woolled Skins

In the coarse-woolled skin the pelt is generally thicker and denser. It is, on this account, usually more valuable. The wool follicles are straight and are inclined at about 45° to the surface of the skin. They are relatively widely spaced and occur individually instead of in clumps. Pelts from the coarse-woolled type of skin are therefore free from pinhole.

The skins of many cross-breds are predominantly either fine-woolled or coarse-woolled in type, and are practically indistinguish-

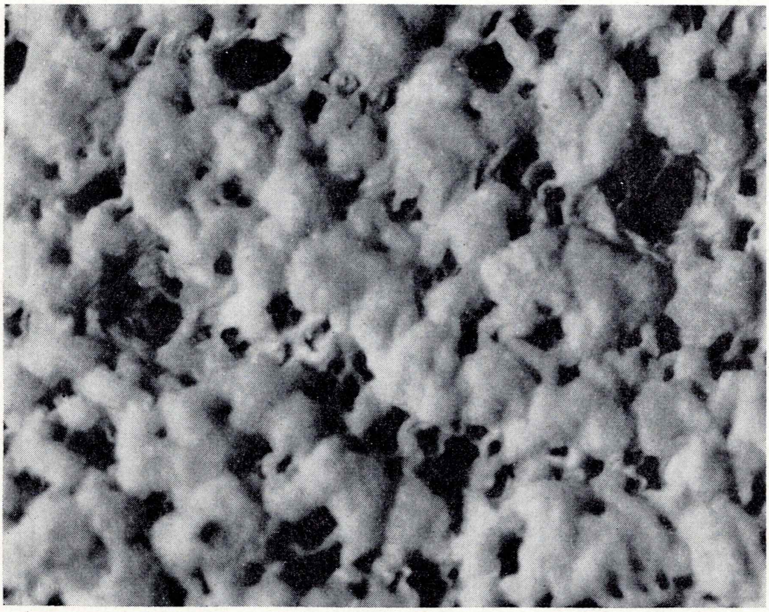


PLATE 6. Pinhole on unfinished chrome-tanned sheepskin

able from those of pure-bred animals. Others are intermediate in character, with wool of varying degrees of fineness and with more or less curved follicles inclined at angles between 45° and 90° to the skin surface. The wool fibres have a greater or lesser tendency to grow in clumps, and the pelts show varying degrees of pinhole. Almost any type of structure between the two extremes may be found in practice.

SEASONAL VARIATIONS

The most important of the seasonal variations as far as the fellmonger is concerned is the change which takes place in the sweat glands. With the hot weather normally experienced in New Zealand in December, January, and February, the sweat glands are called on to secrete large quantities of perspiration in order to keep the animal cool. In consequence, they have to increase considerably in size. In coarse-woolled skins, the glands can, and generally do, develop in the spaces between the wool follicles, but in fine-woolled skins, the wool follicles are so close together that the glands are forced to develop in a layer below the follicles.

Since the sweat glands are destroyed in the process of leather manufacture, a skin with a high proportion of well developed glands will produce a spongy leather, and this effect will be more pronounced in very hot seasons. In the case of fine-woolled skins, the effect can be even more serious. Extreme development of the glands just below the wool follicles often weakens the fibre structure to such an extent that the grain layer becomes almost detached from the flesh layer in places and, in any case, the bond between the two is seriously weakened. Even when, with the advent of cooler weather, the sweat glands shrink again and almost disappear, this weakness persists. Such pelts will be loose grained and very susceptible to mechanical damage. They must be handled very carefully, especially as regards paddling. As we shall see later, there is a tendency even in the best of pelts for the grain layer to part company with the flesh layer if plumping is allowed to take place too rapidly in the lime dolly. With pelts such as we have just described, this tendency is very much more pronounced. Unless extreme care is exercised, such pelts may show quite large areas where the two layers have separated completely.

As would be expected, shorn lambs show less development of sweat glands than do unshorn lambs growing under the same conditions. The shorn lamb can keep cool without sweating so profusely.

VARIATIONS DUE TO SHEARING

The fibre bundles tend to be thinner in a shorn sheepskin than in an unshorn one. On the other hand, as is well known, the skin of a shorn lamb tends to be thicker than that of an unshorn one – no doubt to give the animal added protection and warmth to compensate for the loss of its wool.

Individual skins may show variations of almost every conceivable kind – variations in thickness of skin; proportions of grain and flesh layers; distribution and quantity of fat cells; shape, size, and direction of wool follicles; size and distribution of sweat and fat glands; size and weave of fibre bundles; etc. These variations may be due to differences in breed, health, climate, nutrition, and, above all, to those characteristics which distinguish one individual from another in any race or breed.

SKIN FAULTS

In addition to the variations which occur in the skins of normal, healthy sheep, there are definite faults which appear in skins owing to disease, parasites, injuries, etc. The faults adversely affect the value of the finished pelt, but there is very little the fellmonger can do about them. The main faults of this type are described below. It should be noted that only faults which exist in the skin before it comes into the hands of the fellmonger are discussed at this stage. Faults produced by incorrect fellmongering procedure will be dealt with later.

Scab. This is an injury to the skin caused by a small mite which lives in the wool and bites into the skin to obtain food. The irritation caused by the mites makes the sheep rub against posts or fences, with the result that the affected part soon becomes an open scabby sore. The wool in this area either drops out or assumes a dead-white bleached appearance. The mite is killed by sheep dip, and scab should never occur in a well managed flock. It is rarely seen in New Zealand.

Tick. The tick is another parasite of the sheep which can be controlled by dipping. A ticky sheep is usually in poor condition, and its pelt is consequently small and thin. Inflammation around the tick bites may also cause local damage to the grain of the pelt.

Fly Blow. This damage is fairly well known in New Zealand. It occurs around the butt of the pelt where the grain layer is eaten away in patches. Usually these areas are also badly discoloured.

Cockle. This takes the form of small raised areas which occur most frequently on the flanks and bellies of the pelts. The cockle marks are commonly arranged in rows running at right angles to the backbone, and the raised areas may run together to form ridges. Cockle occurs most frequently in lambs and is seldom seen in sheep. Its cause is not known.

Rape Scald. This appears as a hardened area, yellow to brown in colour, in the middle of the back of the pelt. The affected area is usually smooth, as if the grain pattern had been burned off, and its edges are puckered. The trouble is usually associated with putting sheep on to rape or other heating fodder, and is most prevalent about February or March. The ears of the animal are also badly affected.

Facial Eczema. Toxic substances produced in pasture under certain weather conditions cause damage to the livers of the sheep grazing on it. When this occurs, bile pigments circulate in the blood and are absorbed by the skin, making it very sensitive to sunlight. Consequently, severe sunburn results wherever the skin is exposed to the light, especially around the face and down the middle of the back where the wool is parted. In the pelt, it shows up as a yellowish discoloration down the backbone and around the neck, with eruption of the grain surface. The affected area is tender, and it seems possible that, owing to the presence of the bile pigments, the whole pelt may be adversely affected.

Sunburn. Undue exposure to the sun after shearing will produce sunburn which appears as a yellow or brown discoloration on the pelt. The discoloured area is not so hardened as it is with rape scald and the grain pattern is left intact. It occurs only in sheep and shorn lambs.

Seed. The seeds of certain grasses caught in the wool work their way through to the skin and actually puncture it. The irritation causes small lumps, very much like cockle, except that the puncture marks are plainly visible. The seed itself is frequently still in place in the pelt after it has been pickled.

Shear Marks and Barbed-wire Marks. These are simply the scars left when wounds caused by mechanical injury have healed.

Butcher's Cuts. Careless flaying will produce cuts and scores in the skin, usually in the region of the neck, the butt, and the flanks. The chain system of slaughtering, which necessitates greater use of the knife in freeing the skin from the carcase, has increased the incidence of this damage.

Butcher's Strain. This shows up as a break in the grain of the pelt and is usually found in the flanks. It is caused by too violent tugging of the skin during flaying, and occurs where the skin is gripped by the butcher. The breaks caused by butcher's strain usually run more or less parallel to the backbone, whereas similar breaks caused by the fleshing machine are usually at right angles to the backbone.

Chapter 2

SOME CHEMICAL THEORY RELATED TO FELLMONGERY PROCESSES

The operations which are necessary to convert a raw skin into a pickled pelt are fundamentally a series of chemical processes, and to understand their significance and to control them intelligently, some idea of the underlying chemical theory is absolutely essential. Those of you who have a vague memory of the chemistry you learned at school will find that the knowledge is of very limited use to you, because, unfortunately, the chemistry of the fellmongering processes belongs, in many cases, to the more advanced and complicated branches of the subject. In this chapter, we have therefore started from scratch, and have assumed no previous knowledge of chemistry whatever, although we have assumed that you are familiar with the chemicals used in the fellmongery and with the practical operation of fellmongery processes. The descriptions given of some of the more complicated chemical reactions have been somewhat simplified, in order that the account should be as clear and readable as possible. Strict scientific accuracy has been a secondary consideration, and it has unhesitatingly been sacrificed wherever it would have involved a long and complicated explanation. In general, the descriptions given of chemical reactions are correct as far as they go. They do not always give the whole story, but they should give enough of the story to enable the fellmonger to appreciate more fully the significance of the various processes which he has under his control.

Chemical formulae and mathematical expressions seem, for some reason, to frighten most people. Their use has therefore been avoided in this book, although a list of chemical formulae with their meanings is given in Appendix 1.

INORGANIC AND ORGANIC CHEMISTRY

Chemistry is usually divided broadly into two sections – inorganic and organic. Originally, organic chemistry dealt with those substances which were produced by living organisms – for example, alcohol, sugar, starch, acetic acid (vinegar), fats, vegetable oils, etc. Inorganic chemistry, on the other hand, dealt with substances of more or less mineral origin such as salt, lime, sulphuric acid, caustic soda, sal ammoniac, etc. Nowadays, thousands of organic substances have been made artificially, so that the above definition no longer applies, but the examples which have been given will convey some idea of the type of substance in each division. Organic chemistry is now taken as being concerned with those substances which contain carbon in their make-up. A sheepskin consists almost entirely of organic substances, while the materials which the fellmonger uses in his processing of the skin are mainly inorganic chemicals.

ACIDS, BASES, AND SALTS

Almost all inorganic substances and quite a number of organic ones can be put into one or other of the three classes, acids, bases, and salts. *Acids* are characterised by having a sour taste, by turning blue litmus paper red, and by the way in which they attack many metals such as iron and zinc. Common acids are sulphuric, hydrochloric (often called "muriatic"), boric (also known as "boracic"), citric, and tartaric. The last two are organic acids. *Bases* or *alkalis* are in many ways the opposite of acids. They turn red litmus paper blue, and they "neutralise" or combine with acids to form substances which are neither acid nor alkaline. Well known examples of bases are caustic soda, caustic potash, lime, and ammonia. All of these are inorganic. *Salts* are formed when bases and acids neutralise each other. They usually have a salty taste and are generally, but not always, neither alkaline nor acid. Examples of salts are sodium chloride (common salt), calcium chloride, sodium sulphide, sodium borate (borax), calcium sulphate, magnesium sulphate (Epsom salts), and ammonium chloride (sal ammoniac). The combination of acids and alkalis to form salts is shown in the following table:

Acid	plus	Alkali	gives	Salt
Hydrochloric	+	Caustic Soda	=	Sodium Chloride
Hydrochloric	+	Lime	=	Calcium Chloride
Sulphuric	+	Magnesia	=	Magnesium Sulphate
Sulphuric	+	Lime	=	Calcium Sulphate
Hydrochloric	+	Ammonia	=	Ammonium Chloride
Boric	+	Caustic Soda	=	Sodium Borate

We shall now discuss each of these three groups in rather more detail, because an understanding of their properties is the key to a great deal of the chemistry involved in fellmongering processes.

Acids

If you look carefully at the list of acids given in the paragraph above, you will notice that there is a big difference in properties between the first two (sulphuric and hydrochloric) and the last three (boric, citric, and tartaric). You can put boracic acid in your eye or apply it to a wound, but you certainly could not do either of these things with sulphuric or hydrochloric acid. You could take a mouthful of citric or tartaric acid and, although it would taste unpleasantly sour, it would do you no harm. The same thing could hardly be said of sulphuric or hydrochloric acid. Why this difference?

All acids contain hydrogen in their make-up. This hydrogen is not present as hydrogen gas, of course, but is combined with the other elements which make up the acid. Now, when an acid is dissolved in water, there is a tendency for the hydrogen to split off from the rest of the acid, and to form free-lance particles which the chemist calls "hydrogen ions". This splitting-up process which takes place when an acid is dissolved in water is called "ionisation", and an acid which has split up in this manner is said to be "ionised". The hydrogen ions are still not hydrogen gas and they do not bubble off from the acid solution. When we say that an acid is ionised in solution, we mean that it has split up, and that there are hydrogen ions in the solution of acid and water. Now, only ionised acid has any acidic properties. Only ionised acid will turn blue litmus paper red or will neutralise alkalis. But all acids do not ionise or split up to the same extent. A "strong" acid like sulphuric ionises almost completely, but a "weak" acid like boracic acid ionises only to a very slight degree. Since only the ionised acid is "active" acid, boracic acid will not show marked acidic properties at all. Most of it is in the non-ionised or inactive form. On the other hand, sulphuric acid, being almost completely ionised, will be almost all in the active form and will show very strong acidic properties. Citric and tartaric acids ionise to a greater extent than boric, but not nearly so completely as do sulphuric and hydrochloric acids. They are therefore more acidic than boric acid, but much less so than sulphuric or hydrochloric acid. The explanation of the difference between strong and weak acids is thus a fairly simple one.

It might be as well to digress for a moment at this point, and to define our terms more clearly. We have used the expression "strong acid" to denote an acid which is almost completely ionised and which is therefore mostly in the active form. We have used the expression "weak acid" for one which is only slightly ionised and which therefore contains very little active acid. Unfortunately, the words "strong" and "weak" are quite commonly used in another sense. "Strong" is often used to denote a solution containing a large amount of acid in a small amount of water, irrespective of whether the acid is a strong one like sulphuric or a weak one like boracic. Similarly, "weak" often means a small amount of acid in a large amount of water. Using the terms in two senses like this may lead to confusion. As far as possible in this book, we shall use the word "concentrated" for a solution containing a large amount of a substance dissolved in a small amount of water, and the word "dilute" for a solution containing a small amount of a substance dissolved in a large amount of water. Thus we can have a *concentrated* solution of a *weak* acid or a *dilute* solution of a *strong* acid. With this small point cleared up, let us return to our strong and weak acids.

All this talk of "ionisation" and of "active acid" is not merely of academic interest to the fellmonger. Acids have certain properties which vitally concern him. To take but two examples: acids have the power of causing pelts to "plump" or "swell"; and the growth of both bacteria and moulds is retarded when much acid is present. Both with the plumping and the checking of organism growth the effect depends on the amount of acid present, but note that it is the amount of "active" or ionised acid that matters, not the total amount of acid present. A "strong" acid like sulphuric will have a much greater effect in swelling pelts or in repressing mould growth than will the same amount of a weaker acid like citric or tartaric. With regard to the repression of mould growth, however, we must sound a note of caution. Formic acid, which is not a particularly strong acid, is very effective in repressing mould growth, and prussic acid, which is also fairly weak, is very poisonous to moulds (and to all other forms of life!). The action of these acids is not, however, due to their acidity, but to their other properties. If they had to depend on their acidity alone, they would be less effective than sulphuric or hydrochloric acid.

Thus we see that in certain fellmongering operations what matters is not so much the quantity of acid present, but rather the quantity of "active" or ionised acid present. Since the amount of "active" acid is so important, it would be a decided advantage if we could measure it. At first sight, it might be thought that, since only the "active" acid has acidic properties, only the "active" acid would combine with an alkali, and that therefore the "active" acid could be measured by titrating with standard caustic soda in the same way as you would titrate a pickle liquor. It is quite true that only the active acid will combine with an alkali, but unfortunately there are complications. We said that in the case of a weak acid only a small proportion, say 1 per cent for argument's sake, is ionised. But this proportion stays constant no matter how much or how little acid is present. So, imagine a solution of a weak acid, only 1 per cent of which is in the active or ionised form. The remaining 99 per cent is inactive. You add caustic soda which promptly combines with the active acid and neutralises it. This leaves no active acid in solution, so, to keep the proportion right, 1 per cent of the inactive acid immediately changes to the active form. The new active acid is neutralised by the caustic soda, so once again 1 per cent of what now remains of the inactive acid must change to the active form to keep the proportion right. And so the process goes on with the acid trying to keep 1 per cent of the active form in solution and the caustic soda neutralising it as soon as it appears. In the end, of course, the whole of the acid is first of all converted to the active form and then neutralised by the caustic soda. Titration therefore measures not the amount of ionised or active acid originally present, but the total acid, both active and inactive. A strong acid will neutralise only the same amount of caustic soda as will the same quantity of a weak acid, even although the strong acid may contain 100 or even 1,000 times as much active acid as the weak one. Titration with standard caustic soda is therefore useless as a measure of the active acid in a solution. There are methods which can be used to measure the active acid, but we shall leave them until a later section of this chapter.

The acid which the fellmonger has to deal with most commonly is *sulphuric acid,* and it might be as well to mention a few extra facts about it. The commercial acid which is supplied either in bulk or in jars from fertiliser works is an oily liquid with a specific gravity of about 1·7. This means that it is more than half as heavy again as water. A gallon of sulphuric acid weighs about 17 lb, whereas a gallon of water weighs only 10 lb. But commercial sulphuric acid contains only about 70 per cent of pure sulphuric acid. The other 30 per cent is water, apart from a few minor impurities which are usually of no concern to the fellmonger. In making calculations, it is necessary to remember this 70 per cent strength, because chemical calculations are made on the basis of pure 100 per cent acid.

Bases

As we said earlier, bases or alkalis are in some respects the opposite of acids. They neutralise acids and remove their acid properties. But alkalis resemble acids in that there are "strong" ones such as caustic soda and "weak" ones such as ammonia. Once again, this difference is due to the change known as "ionisation" which takes place in solution, and once again, the highly ionised bases such as caustic soda are the "strong" ones, while the feebly ionised bases such as ammonia are the "weak" ones. Lime, in which the fellmonger is particularly interested, is a moderately strong alkali. It is stronger than ammonia but is weaker than caustic soda. We have already mentioned that acids, when they ionise, form *hydrogen ions*. Bases or alkalis, on the other hand, form *hydroxyl ions*, and these hydroxyl ions are characteristic of alkalis, just as hydrogen ions are characteristic of acids. As with acids, it is impossible to measure the "active" base in a solution by titrating it with standard acid. A weak base, like a weak acid, tries to keep a fixed proportion in the active form, and replaces it as fast as it is neutralised by the acid. Titration therefore measures the total base present, and not just the active base.

In the case of lime, there is an added complication. Lime is not very soluble in water, so that even in a saturated solution there is not a great deal of total alkali, and of this total alkali, only a portion (about 60 per cent) is in the active or ionised form. A lime solution can therefore never become very strongly alkaline, partly because very little of the lime can dissolve, and partly because a considerable proportion of what does dissolve is in the inactive form. But consider what happens when you titrate with standard acid, a lime solution which contains extra lime in suspension as well. When the acid is added, the active lime will be neutralised and some of the inactive dissolved lime will change over to the active form to take its place. But since the active lime has been neutralised, the *total* amount of lime in solution has been reduced, and some of the undissolved suspended lime will now dissolve to keep the solution saturated. This sequence of events, neutralisation of the active lime, conversion of inactive dissolved lime to the active form, and dissolving of the suspended lime, will go on until all the lime, active, inactive, and suspended, has been neutralised by the acid. This is because, during the whole time, the solution is trying to keep itself saturated with dissolved lime, and also to keep 60 per cent of the dissolved lime in the active form.

Now the situation in a lime dolly is very much like that described in the last paragraph. The lime liquor is saturated with lime and also contains additional lime in suspension. The pelts themselves can absorb and neutralise lime, and can thus act in the same manner as an acid. One of the objects of liming is to produce an alkaline condition in the pelts, but the alkalinity must not be too great or damage to the pelts would result. With suspended lime present in the lime liquor, we can be sure that as fast as the dissolved lime is neutralised by the pelts, it will be replaced by suspended lime which will dissolve to keep the liquor saturated. We have already seen that a lime solution can never become strongly alkaline, so that by its use in a lime liquor it is possible to maintain a steady, moderate alkalinity quite automatically even although the pelts are using up lime.

The Meaning of pH

We are now in a position to deal with the meaning of the term "pH", of which most of you will have heard at one time or another. pH is simply a measure of the "active" acidity or "active" alkalinity of a solution. More strictly, it is a measure of the concentration of hydrogen ions in a solution, but, as we have mentioned above, when an acid ionises it produces hydrogen ions, and the more it ionises, the more hydrogen ions it produces. Therefore the concentration of hydrogen ions in an acid solution is a measure of its degree of ionisation or of its "strength". We mention this because you may come across the term "hydrogen ion concentration" in connection with pH, and wonder what it means. We shall continue to refer to pH as a measure of the active acidity or alkalinity and shall forget about "hydrogen ions" in the meantime.

For reasons which we shall not go into here, but which are very good ones, the pH scale runs in the opposite direction to the active acidity. A high concentration of ionised or active acid means a low pH and *vice versa.* In this respect, the pH scale resembles the Standard Wire Gauge system in which the biggest wires are given the smallest number. For acids, the pH scale runs from 0 to 7, 0 being very strongly acid, while 7 is neutral. A concentrated solution of a "strong" acid like sulphuric acid has a pH value very close to 0. Pure water, being neither acid nor alkaline, has a pH value of 7. Until you get used to it, the pH scale is rather deceptive, not only because a low pH means a high acidity, but also because each pH unit less means a tenfold increase in the active acidity. Thus, a solution with a pH value of 1 has 10 times as much active acid as a solution with a pH value of 2, 100 times as much as a solution with a pH value of 3, and 1,000 times as much as one with a pH value of 4. A change from pH 1 to pH 4 may not sound very much, but it represents a thousandfold decrease in the active acidity.

To give you an idea of the variation of pH value with the strength (not the concentration) of acids, we can illustrate the point with acids with which you are familiar. Ordinary vinegar is a solution of acetic acid together with flavouring and colouring matter which it has picked up from the malt We can consider it merely as a solution of acetic acid. If you took vinegar and diluted it down with six times its own volume of water, you would get an acid solution with a pH value of about 3. This is not very strongly acid; in fact, it is much less so than the mint sauce to which you freely help yourself when it appears on the menu with lamb and green peas. But if, instead of acetic acid, you made up a solution containing the same amount of hydrochloric acid, you would get a solution with a pH value of about 1, and this would be very strongly and unpleasantly acid indeed. On the other hand, if you used the same amount of boric acid instead, you would get a pH value of about 5. This would hardly appear acid at all, and you could use it in an eye-bath. Now, the point to notice particularly is that if you titrated these three solutions with standard caustic soda, you would get the same result in all three cases. Although these three solutions all contain exactly the same amount of *total* acid, the hydrochloric acid solution contains 100 times as much *active* acid as the acetic acid solution and 10,000 times as much as the boric acid solution.

You can look at this in another way. Taking the three acid solutions which we considered in the last paragraph, you would have to dilute the hydrochloric acid solution down 100 times to bring it to the same pH as the acetic acid solution. It would then contain the same amount of *active* acid as the acetic acid solution but only one-hundredth as much *total* acid In the same way, if the hydrochloric acid solution were diluted down 10,000 times, it would have the same pH value (5) as the boracic acid solution, although titration would show that the boracic acid solution contained 10,000 times as much *total* acid.

The same pH scale serves for alkalis as well. Since pH 7 is neutral, the alkaline scale runs, as you would expect, from 7 to 14. This gives a complete scale of decreasing acidity or, if you prefer it, of increasing alkalinity from 0 to 14. pH 0 is very strongly acid, pH 7 is neutral, and pH 14 is very strongly alkaline. As with the acids, an increase of one pH unit means a tenfold increase in *active* alkalinity. An alkaline solution of pH 11 has 10 times as much *active* alkali as one of pH 10 and 100 times as much as one of pH 9. As an indication of alkaline pH values, a saturated solution of lime has a pH value of just over 12, while a ½ per cent solution of caustic soda has a pH of about 13.

We can now consider briefly the question of measuring pH values. In some cases we can use substances called "indicators" which have the convenient property of changing colour with change of pH. One of these indicator substances with which you are all familiar is phenolphthalein; another is litmus. Phenolphthalein is colourless in acid solution. It starts to turn pink at pH 8·3, becomes gradually more intensely red as the pH rises, and reaches its full red colour at pH 10. Between pH 8·3 and pH 10 the depth of colour of phenolphthalein would indicate the pH value of the solution. There are other indicators which change colour over different pH ranges, so the method is quite a useful one generally, but unfortunately it is not reliable in the presence of salts or protein matter. In the fellmongery almost all the solutions we want to test contain both salts and protein matter, so the indicator method is not of much use to us if we want really accurate results. It is very useful, however, if we want a quick test for the approximate pH value. Phenolphthalein can be put on the cut edge of a pelt to indicate the progress of deliming, and test papers, which consist of filter paper impregnated with an indicator, can be used as a rough check to see whether the pH of a bate dolly is low enough for bating action to take place.

Of all the methods of pH measurement, the only one of much practical use in the fellmongery when accurate results are required is the *glass electrode pH meter*. This type of pH meter is an electrical instrument whose action is too complicated to explain here. Its use in practice is, however, quite simple, and it is generally only a matter of pressing a button and leaving the gadgets inside the box to give you the right answer. The pH meter is a fairly delicate instrument and there are some pitfalls in its use which may trap the unwary. It is usual therefore to leave its operation and care in the hands of the chemist.

Although the account given above is a very much simplified explanation of the meaning of pH value, it is not essential that you should memorise even this small amount of information. All that you really should remember is given in the following summary:

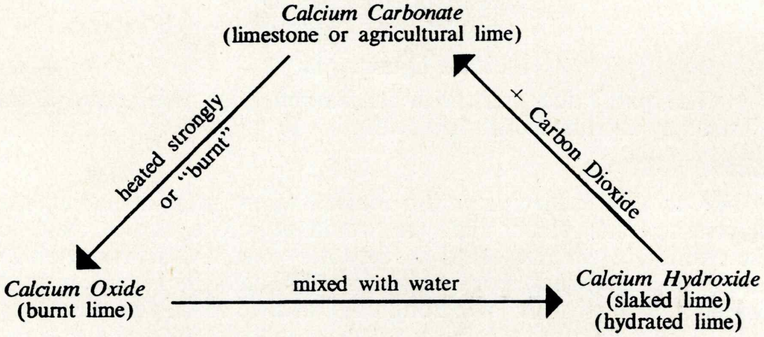
> The pH value of a solution is a measure of its *active* acidity or alkalinity, and this is not necessarily the same as its *total* acidity or alkalinity as measured by titration. It is the pH value and not the total acidity or alkalinity which determines whether a solution will cause pelts to plump, or will allow an enzyme bate to do its work, or will prevent the growth of moulds and bacteria. The pH scale runs from 0 which is very strongly acid, through 7 which is neutral, to 14 which is very strongly alkaline. The following list gives a rough indication of the properties of solutions at various pH values:
>
> pH 0: very strongly acid
> pH 3: moderately acid
> pH 5: very weakly acid
> pH 7: neutral
> pH 9: weakly alkaline
> pH 12: moderately alkaline
> pH 14: very strongly alkaline
>
> Approximate pH values in round numbers of the solutions used by the fellmonger are:
>
> Lime liquor: pH 13
> Bate liquor: pH 9
> Pickle liquor: pH 2
>
> The pH values met with in fellmongering thus range from strongly alkaline to strongly acid.

Salts

As we saw earlier, salts are formed when an acid and a base neutralise each other, and you would therefore expect them to be neutral in reaction. And so they are when the acid and alkali are both strong ones. For instance, sodium chloride (common salt) which is formed from the strong base, caustic soda, and the strong acid, hydrochloric acid, give solutions which are quite neutral. So does sodium sulphate (Glauber's salts) which is made from caustic soda and sulphuric acid. But sodium carbonate (better known as "washing soda" or "soda ash") is made by the combination of caustic soda, which is a strong base, and carbonic acid, which is a weak acid. When sodium carbonate is dissolved in water, the strongly alkaline part overwhelms the weakly acidic part, and the result is an alkaline solution. But the acidic part does reduce the alkalinity to some extent, and soda ash is a milder alkali than caustic soda. A solution containing 0·2 per cent of soda ash has a pH of about 11, whereas a similar solution of caustic soda has a pH value of above 12. Since a high pH is damaging to wool, it is safer to use soda ash rather than caustic soda for wool scouring.

In the case of sodium carbonate, we can reduce the alkalinity still further by treating it with more carbonic acid. This produces a salt called sodium bicarbonate (commonly known as "baking soda") which contains twice as much carbonic acid as does washing soda. It is still alkaline, but much less so than washing soda.

Calcium carbonate or limestone is a salt which the fellmonger meets in the form of "lime blast" on his pelts, and is produced by the action of the carbonic acid (carbon dioxide) in the air on the lime from the paint used as a depilatory. Being a combination of a moderately strong base with a weak acid, it is also alkaline, but it cannot show its alkalinity in solution because it is insoluble in water. Its insolubility, of course, accounts for the difficulty of removing lime blast from pelts. You may find that the common names for these lime compounds is sometimes confusing. Calcium carbonate is often referred to commercially as "lime" although it is quite different from the calcium hydroxide, which is the "lime" of the fellmonger, and from the calcium oxide, which is the "burnt lime" used for making mortar. These are three distinct substances although they can be made from each other as follows:



So be sure that when you use the term "lime", you make it quite clear which substance you mean.

The sodium sulphide which is used in depilatory paint is another example of a salt formed from a weak acid and a strong base. It, too, gives an alkaline reaction. If we double up on the acid used in its formation, we get another salt called sodium hydrosulphide or sodium sulphydrate, in the same way as we got baking soda from washing soda. Sodium hydrosulphide is much less alkaline than sodium sulphide. In fact, sodium sulphide in solution is roughly equivalent to a mixture of equal parts of caustic soda and sodium hydrosulphide. We shall deal with this more fully in the chapter on painting and liming.

Ammonium chloride (sal ammoniac) is an example of a salt formed from a strong acid and a weak base. It is made from ammonia, which is a weak base, and hydrochloric acid, which is a strong acid. Consequently, its solutions are very weakly acidic. A solution containing $\frac{1}{2}$ per cent sal ammoniac has a pH of about 6. This property makes it a very safe deliming agent as we shall see later. No matter how much sal ammoniac is present, the pH can never fall low enough (that is, the liquor can never become strongly acid enough) to damage the pelts.

You should also note that a strong base can displace a weaker base from one of its salts. Lime is a stronger base than ammonia. Consequently, when you add ammonium chloride (sal ammoniac) to limed pelts, the lime displaces the ammonia and seizes the chloride for itself. The result of this is that:

ammonium chloride + lime = calcium chloride + ammonia.

This chemical reaction is the basis of the normal deliming method. In the same way, caustic soda is a stronger base than lime. If calcium chloride is added to depilatory paint or to a lime dolly containing caustic soda derived from sodium sulphide, the caustic soda will displace the lime from the calcium chloride and will combine with the chloride to form sodium chloride (common salt):

caustic soda + calcium chloride = sodium chloride + lime.

This is the principle behind the addition of calcium chloride to depilatory paint to reduce its alkalinity. The strongly alkaline caustic soda goes into combination and the much less alkaline lime is left in its place.

Salts have another property which may be mentioned at this stage. They can hold on to, or "bind", water so that it is not available for other purposes. For example, bacteria, like all living organisms, need water for their life processes. Salts can "bind" the water so that it is not available to the bacteria. Although there may be plenty of water present, the bacteria cannot use it if salts are present as well. It is this property of salts which makes it possible to preserve foodstuffs in brine or by salting them. The bacteria die for lack of water. In the same way, in certain conditions which we shall describe later in this chapter, pelts will swell or plump by absorbing water. If salt is present, however, this swelling or plumping is retarded or even prevented altogether even when the other conditions are favourable.

PROTEINS

The realm of organic chemistry is a vast one, but the fellmonger is interested mainly in only one small section of it – the proteins. The proteins are rather hard to describe in non-scientific language, and it will be simpler to illustrate their nature by means of examples. In the first place, they are found only in living organisms; the chemist has not yet been able to synthesise them, much as he would like to be able to do so. If you take away the fat, the water, and the bone from almost any animal tissue, what you are left with is mostly protein. Skin, hair, wool, sinews, and the lean part of meat are all made of protein. Egg white is almost pure protein, so is gelatine, and so is the casein of milk. Apart from water, cheese is about half protein and half butterfat. As you will have noticed, proteins vary tremendously in their properties, from egg white and gelatine which dissolve in water to give more or less sticky solutions, to skin, sinew, muscle, and wool which are insoluble in water and which are very strong and tough.

From the chemical point of view, proteins are rather tricky substances to deal with. Violent treatment of any sort is liable to do them permanent damage. Heat, for instance, is particularly dangerous. You are all familiar with what happens to egg white when it is boiled, and this change of properties is permanent; there is no known way of "unboiling" an egg. Other proteins, including those in the sheepskin, are equally liable to damage by heat, but in the case of the skin proteins, heat causes the fibre structure to break down and also causes the individual fibres to lose their toughness and strength.

Proteins have the remarkable property of being able to combine with and neutralise both acids and alkalis, but their powers of doing so are not very great. Of the acid added to the pickle dolly, a certain amount is taken into combination by the proteins of the pelts and is neutralised by them, but this amount is very limited. Acid or alkali in excess of the amount which can combine with the proteins tends to attack them and break them down. Most proteins are fairly stable at pH values round about the neutral point. They are attacked only slowly and slightly by mild acids and alkalis, but the rapidity and severity of the attack increases as the strength of the acid or the alkali increases. In other words, proteins are rapidly and permanently damaged at very high and very low pH values. In most cases, and this applies to the skin proteins, moderately strong acids and alkalis produce only a temporary change in the properties of the protein, which returns to its original state when the acid or alkali is neutralised. This is not the case, however, when the action of the acid or alkali is too prolonged or, more particularly, when the temperature is too high. Even mild acids and alkalis can do permanent damage when the temperature is allowed to rise and, of course, stronger acids and alkalis are particularly dangerous at high temperatures.

You have probably all seen what happens to painted skins or limed pelts when they have become heated. With regard to the action of acid and alkali on protein, please remember that, once again, it is the pH which matters – not the *total* acid or alkali present.

This should give you some idea of the properties of proteins in general, at least in so far as they concern the fellmonger. We shall have more to say later about the special properties of the skin proteins, and in the chapters dealing with the processing of pelts we shall describe the changes which take place in the skin proteins at each stage of the working.

ENZYMES

Although mild acids and alkalis attack proteins only very slowly and to a very limited degree, there are substances which, by their action, can speed up and intensify the attack. These substances are *enzymes*. Enzymes are substances which enable chemical reactions to take place rapidly, when otherwise they would take place only very slowly if at all. They are remarkable in that they themselves are not used up in the process, and can continue to act almost indefinitely. Enzymes are rather like the oil in a machine. Without the oil, the machine would seize up and refuse to run, but with the oil the machine runs easily and rapidly. Yet the oil is not used up by the machine, and if it does not leak away, will continue to act almost indefinitely. There are enzymes which can help along almost every chemical process which takes place in the living organism, and without them life would be impossible. But the only enzymes we are interested in here are those which aid in the breakdown of proteins They are called "proteolytic enzymes", in case you should meet the term.

Proteolytic enzymes, then, are substances which enable mild acids and alkalis to break down proteins when the acids and alkalis would be quite unable to do so by themselves. There are numerous proteolytic enzymes, each of which has its own peculiarities. Some will break down one protein but will not attack others. Some will act only in an acid solution, while others can be used only in alkaline conditions. In the fellmongery we are concerned with only one proteolytic enzyme and that is *trypsin* which can be obtained from the pancreas glands of animals and from certain moulds and bacteria. Trypsin is the active constituent of enzyme bates, and it acts most effectively at pH values between 8 and 9. A solution in this pH range is certainly alkaline, but not nearly alkaline enough to attack protein unaided. The addition of trypsin to the bate liquor disperses skin proteins which have already been degraded in the liming process.

THE CHEMISTRY OF THE SKIN

We have already dealt with the structure of the skin, and we are now in a position to consider the chemical properties of the skin constituents. Raw skin contains from 50 to 70 per cent of water which is therefore its main constituent. We are not particularly concerned with the water at this stage, however. Skin also contains a considerable but variable amount of fat. We do not propose to add anything here to what we said about fat in Chapter 1. There is also about ½ per cent of mineral matter, mainly salt, but this is of little importance to the fellmonger. Of the solid matter in the sheepskin, by far the greatest bulk consists of protein matter, and this protein matter is the prime consideration of both the fellmonger and the tanner. Easily the most important protein in the skin is the one known as *collagen,* but others which merit some attention are *keratin,* which is the main constituent of wool and epidermis, *elastin,* the *mucins,* and the problematical *reticulin.*

Collagen

Collagen is the main constituent of the unit fibrils and fibres which, as we saw in Chapter 1, make up the true skin or dermis. Collagen is known as a fibrous protein because it occurs in long, strong threads. It is quite insoluble in water, but like most proteins, is slowly attacked by weak acids and alkalis, and rapidly by strong ones. It is, however, more resistant to acids than it is to alkalis. Trypsin attacks collagen in weakly alkaline solution, but the attack is not at all severe. During the very short bating which the fellmonger gives his pelts, there is no time for the trypsin to have any real effect on collagen which has not already been degraded in the lime dolly. If the unit fibrils of collagen have become filamented, however, trypsin will attack them readily.

From the fellmonger's point of view, probably the most important property of collagen is its power of plumping or swelling by absorption of water when it is placed in either acid or alkaline solutions. The degree of absorption depends on the pH of the solution. At very high and very low pH values, the collagen is permanently damaged if left in contact with the solution for any length of time, but at moderate pH values it returns to its original state, and the pelt "falls" when the acid or alkali is neutralised. At pH values likely to occur in the fellmongery, from the acid pickle dolly to the alkaline lime dolly, the effect of pH on the swelling of collagen can be represented by the graph given in fig. 2.

The swelling of collagen when placed in liquids of various pH values is shown as a continuous line in fig. 2. We see that there are two points of maximum swelling, one around pH 2 and the other around pH 12. These correspond to the points in our processing of pickling and liming. You may ask why the curve does not rise further as we approach pH 1. The answer is that the structure of the collagen begins to give way in the presence of so high a concentration of active acid and the swelling breaks down. The swelling is quite different when salt is added to these solutions at the various pH values. The broken line in fig. 2 shows what happens in the presence of 12 per cent of salt. You will note that the swelling at pH 2 is completely suppressed. This explains, of course, why pelts do not swell in pickle liquor which, as we mentioned earlier, has a pH of about 2. On the alkaline side the salt reduces the swelling, but not in nearly so marked a fashion as it does on the acid side.

The effect of the salt is due, of course, to the "binding" of the water by the salt as we mentioned earlier in this chapter. The water is not available to the pelt, and swelling cannot take place. If you are interested, put a piece of delimed pelt into 1 per cent sulphuric acid without any salt and see the enormous amount of swelling which takes place.

On the alkaline side, there is one added factor to take into account. The amount of swelling is dependent not only on the pH but also, to some extent, on the nature of the alkali present. Caustic soda will cause much more intense plumping than lime will at the same pH. We have already mentioned that sodium sulphide in solution produces caustic soda and sodium hydrosulphide. Therefore, if sodium sulphide is present in solution, caustic soda is also present. Since caustic soda is such a powerful plumping agent, the use of sodium sulphide in modern rapid liming methods means that much more care must be taken with the pelts if mottle and similar damage is to be avoided. This point will be elaborated in the chapter on liming.

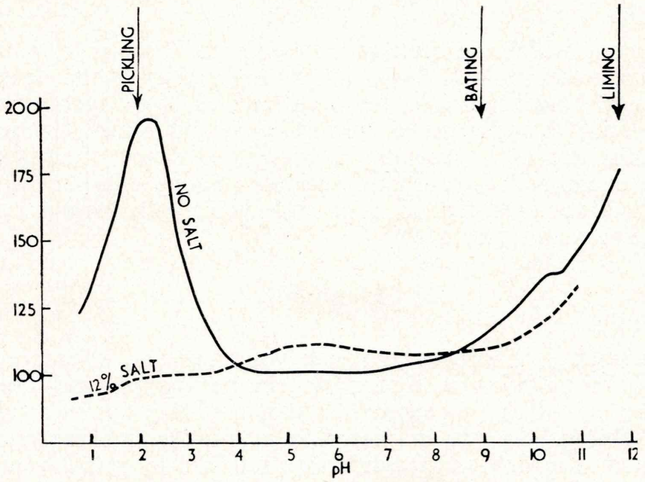


FIG. 2.

The various fellmongering operations are marked on fig. 2. Painting and liming take place around pH 12–13. The painted skin is not swollen to any extent because there is not sufficient water to swell it, but in the lime dolly the skin is swollen to an extent represented by the continuous line in fig. 2 at pH 12. During deliming and bating, the lime is neutralised and the pelt falls or loses water. The pH falls to the region of pH 8–9 and the volume of the pelt follows the continuous line in fig. 2 down to that region. In the pickle dolly, salt is present, and the volume of the pelt now moves on to the broken line at pH 2. Due to the presence of the salt, it does not swell, but remains fallen and flaccid.

Keratin

Keratin is the basic constituent of wool, hair, epidermis, and even of such harder structures as nails, horns, and claws. Keratin is particularly resistant to water, to weak acids and alkalis, and to such solvents as alcohol and ether. This resistance to attack is the reason for its effectiveness as a protective outer coating over the bodies of animals. But keratin is peculiarly susceptible to attack by sodium sulphide or sodium hydrosulphide in alkaline solution, even although the other skin proteins are unaffected by these reagents. By this fortunate chance, sodium sulphide can be used by the fellmonger to attack and destroy the wool and epidermis which the tanner does not want, and yet leave intact the proteins of the skin which he does want.

Elastin

Elastin, which we referred to briefly in Chapter 1, is also a fibrous protein which forms about 1 per cent of the dermis. It serves to hold in position the fibre bundles of collagen as well as the glands, blood vessels, hair follicles, and other structures of the skin. Elastin is insoluble in water and does not swell to the same extent as does collagen in acid or alkaline solution. Although elastin is very resistant to acids and alkalis, it is readily attacked by the enzyme trypsin.

Reticulin

Reticulin is a substance which you may find reference to in textbooks as being a fibrous protein helping to hold the fibre bundles of collagen together. It is very doubtful, however, whether this substance occurs in sheepskin at all. As was mentioned in Chapter 1, what was thought to be reticulin is probably only an immature form of collagen.

Mucins

Mucins are proteins, but not fibrous ones. They are more like the white of egg, and form the interfibrillary tissue or "cementing substance" which fills the spaces of the fibrous network of the skin, as has been described in Chapter 1. Mucins are insoluble in water but they are swollen by it. They are readily attacked by even very dilute alkalis, and a plain lime solution will disintegrate them quite rapidly. Liming therefore renders them soluble and they can then be removed during deliming and bating. Mucins dry to a hard, brittle mass which is responsible for the texture of dried sheepskins. If they are dried slowly and carefully, the mucins can reabsorb water to resume their normal condition, but if dried too rapidly or at too high a temperature, they become permanently hardened. Most fellmongers are familiar with the difficulty of "soaking back" skins which have been carelessly dried. A small amount of an alkali such as soda ash added to the soak water softens the skins more rapidly by attacking the mucins.

Shrinkage Temperature

There is a property of skin, pelt, and leather which it is convenient to mention at this point although it is not strictly a chemical property. When any of these three materials is placed in water and the temperature of the water is raised gradually, there comes a point where the material suddenly contracts or shrinks. The temperature at which this occurs is usually quite well marked and is known as the *shrinkage temperature*. It is expressed in degrees Centigrade.

The shrinkage temperature is a very useful measure of the strength of the fibre structure. The lower the shrinkage temperature, the weaker the structure. Typical shrinkage temperatures of the materials with which we are concerned are:

Raw, unprocessed sheepskin, about 60°C (140°F).
Freshly pickled pelt, above 52°C (126°F).
Vegetable tanned leather, 70–87°C (158–188°F).
Chrome tanned leather, 77–100°C (170–212°F).

You will notice that pelts have a lower shrinkage temperature than the raw skin. This is because the interfibrillary matter has been removed and the structure has been opened up, thus allowing the water to penetrate and be absorbed by the collagen fibres. Some of the chemical bonds have also been broken during processing. Fellmongery operations, although they weaken somewhat the general structure of the original skin and lower its shrinkage temperature, do not, if properly carried out, have any detrimental effect on the strength of the collagen framework of the skin which is the basis of the finished leather. If, on account of faulty processing, the fibre structure of the pelt has been weakened, it will show up as a lowering of the shrinkage temperature of the pelt.

A properly worked pelt should have a shrinkage temperature of between 54 and 58°C (129°F and 136°F). If the shrinkage temperature is below 52°C (126°F), the pelt will not make sound leather.

Tanning materials combine with the pelt fibres and bond them together. Tanning therefore raises the shrinkage temperature very considerably, and heavily chrome-tanned leather does not shrink even when immersed in boiling water. In other words, its shrinkage temperature is above 100°C (212°F).

This brief summary of chemistry as applied to fellmongering operations is necessarily very sketchy and is far from complete. Only those sections of the subject which have a direct bearing on actual fellmongering processes have been mentioned, and we shall be referring back to this chapter as we deal with the processes themselves in the following pages. A little time and effort spent in mastering the main points in this chapter will, it is hoped, be amply repaid by a better understanding of the more practical side of fellmongering.

Chapter 3

DEPILATION AND LIMING

In the tanning of hides and calfskins, unhairing takes place during liming, and the two processes are thus carried out in one operation. Tannery textbooks, therefore, almost invariably deal with depilation as being merely one of the functions of the liming process. Wool, unlike cattle hair, is a valuable product and must be recovered as nearly as possible in an undamaged state. The fellmonger cannot, therefore, simply put his woolled skins into a lime dolly and let the lime liquor remove the wool at the same time as it limes the pelts. For him, depilation and liming are two separate and distinct operations. Nevertheless, there is a close relationship between the two. The type of depilatory paint used has a profound effect on the pelts, quite apart from its action on the wool roots, and it would not be an exaggeration to say that liming of the pelt starts from the moment the paint is applied to the skin. Because the chemicals used for depilation are the same as those used for liming, and because their nature and strength affect both processes simultaneously, we shall follow tannery practice and deal with both operations in the one chapter.

OBJECTS OF LIMING

Since there is a greater risk of spoiling good pelts during depilation and liming than at any other stage of processing, these two operations are, without doubt, the most important ones in the fellmongery. It would be as well if, at the outset, we understood clearly what we are trying to accomplish in these two processes. The objects of liming may be briefly stated as follows:

(i) To remove the hair or wool from the skin. This may be done during liming, as in the case of hides, or in a separate operation, as in the case of sheepskins. But even with sheepskins there are usually remnants of wool to be removed in the lime dolly.

(ii) To remove the epidermis or "scud", as it is known in New Zealand. Overseas the term "scud" is used rather differently. As was explained in Chapter 1, the epidermis is the outermost layer of the skin, and is valueless for the making of leather.

(iii) To swell and plump the collagen fibres and fibrils. This opens up the fibre structure and allows the chemicals used in subsequent processing to penetrate and gain access to the fibres.

(iv) To modify the non-fibrous proteins and mucous substances in such a manner that they are readily dispersed and removed during deliming and bating. This interfibrillary matter must be removed before tanning, to enable the tan liquors to reach the collagen fibres. Liming is the first stage in the removal of these substances, and efficient bating is not possible on unlimed skins.

(v) To destroy nerves, blood vessels, muscles, and glands which occur in the raw skin, but which are undesirable in the finished leather.

(vi) To weaken the membranes surrounding the fat cells and thus to facilitate degreasing of the pelt during tanning.

(vii) To swell the fatty connecting tissue so that it can be more easily removed by the fleshing machine.

(viii) To break down the sheaths and garters which surround the fibre bundles of collagen. This gives rise to splitting and separation, both of which are desirable in a pelt if not carried too far.

HISTORICAL

Before proceeding with a detailed study of modern methods of depilation and liming, it may be both interesting and instructive to survey briefly the history of the processes and to note what alternative methods have been used and proposed.

When man first conceived the idea of using the skins of animals as clothing, he merely dried them to prevent putrefaction, and then rubbed them with fat or oil to make them soft and pliable. Rawhide made in this way is still used today, especially by primitive peoples. Vegetable tanning of leather, however, was practised even in prehistoric times, and the advantages of liming prior to tanning must have been discovered at a very early date. It is certainly mentioned in the earliest written records. The use of a sulphide, although not sodium sulphide, as a depilatory has also been known for a very long time. A depilatory paste of quicklime and arsenic sulphide is mentioned in the *Arabian Nights*.

Depilation and liming by means of a straight lime liquor was the normal procedure from ancient times right up till about the middle of last century. In many cases, the lime liquors were used for months without being renewed. Such lime liquors, apart from being evil-smelling and unpleasant to work with, were most uncertain and capricious in their action, owing to the variability of their composition.

About the middle of last century, it was found that spent lime from gasworks gave very good results when added to lime liquors. This lime had been used to free the gas from sulphur compounds, and it therefore contained considerable quantities of sulphides which, of course, aided both depilation and liming. Soon after this, the large-scale manufacture of sodium sulphide was started, and the use of this substance has continued up to the present day.

OTHER DEPILATORIES

Besides the widely used lime and sodium sulphide paint, a large number of other substances can be used to dewool or unhair skins. Quite a number of acids, particularly acetic acid (the acid in vinegar) and formic acid, will act in this way. Of the alkalis, ammonia is particularly effective. No large-scale process has yet been developed using any of these chemicals, but it is quite possible that future progress may be made along these lines. There are, however, two methods of depilation which have been used on a commercial scale, although not in New Zealand. We shall give a short account of them before going on to a fuller consideration of the conventional painting method.

Sweating

This method is still used, especially in Australia and France, on a large though diminishing scale. The skins are hung up or stacked in a damp, warm atmosphere for three or four days, during which time the wool or hair is loosened by bacterial action. The process is thus a mild form of "pieing" and is equally malodourous. It is not without advantages, however, especially when dealing with Merino skins. In sweating, the wool fibre is not attacked at all. It is the sheath surrounding the fibre which is destroyed, and the whole fibre, including the root, is recovered. Lime - Sodium-sulphide paint, on the other hand, destroys or severely damages all of the wool fibre lying below the skin surface, and in many cases damages some of the fibre above skin level, too. The Australians have estimated that on the average, sweating gives about a 5 per cent greater yield of wool than does painting. With such a valuable product as Merino wool, this is an important consideration. On the other hand, sweating damages the pelt to a greater extent than does painting. The Merino pelt, however, is a relatively poor one in any case, and this consideration is not so important as it would be with our New Zealand skins. But the sweating process is difficult to control accurately, as well as being most unpleasant for the workers, and it is gradually being replaced everywhere by the painting process.

Enzyme Depilation

During the last few years, especially on the Continent, the use of proteolytic enzymes as depilatories has made some progress, but, since most of our information here is derived from advertising literature, it is difficult to judge to what extent the process has been adopted commercially. Many of the enzyme depilatories are of German origin and are prepared from moulds or bacteria. A large number of commercial bates are, of course, prepared in the same way. The enzyme depilatories are applied to the flesh side of the skin, either as a paste which is painted on in the normal manner, or as a powder which is dusted on.

Australian workers have made quite a study of these enzyme depilatories. Their tests were made on small pieces of skin in the laboratory and were designed to find out which moulds and bacteria gave the most active enzymes. The enzyme which they found to be most effective was the one used in some of the German commercial preparations.

German enzyme depilatories, both paste and powder, have been tested in New Zealand on whole lambskins. In all cases, the depilatory was left on the skins for 24 hours before pulling, as leaving it on for longer periods did not improve the pulling. When the painted skins were held at ordinary temperatures, the results were poor, and reasonable results could be obtained only by holding the skins at 90°F for the whole 24 hours. Even then the pulling was irregular. Although the bulk of the skin pulled well, there were always patches where the wool was still held tightly. Some of these tight patches were over meat or fat on the flesh side, but for others there was no discernible cause. The necessity for heating the skin cellar and the irregularity of the pulling makes any of the present enzyme depilatories unsuitable for New Zealand practice.

LIME - SODIUM-SULPHIDE DEPILATION

In spite of the disadvantages which will become more apparent as we go on, the use of a lime - sodium-sulphide paint followed by a lime - sodium-sulphide liming is by far the most common method of processing sheepskins today. It came into use in England about the middle of last century and was introduced into New Zealand before 1890. According to Australian writers, however, the method was not employed there until about 1914. The process is relatively cheap, relatively clean, relatively effective, and relatively easy to control. When used in a small-scale fellmongery or tannery where the paint can be applied very carefully, where meat and fat can be thoroughly removed from the flesh side of the skin before painting, where the skins can be sorted as to type and the paint varied to suit each type, and where pulling can be delayed for a few hours if the skins are not quite ready, the painting process can give excellent results. In a New Zealand freezing works where none of these conditions apply, the results leave much to be desired. But it is the best process we have at the present time, and it therefore merits our close attention. A thorough understanding of the process will enable us to avoid its worst faults, or at least to lessen their effect.

The Action of Sulphide in Paint

We mentioned in our description of the skin proteins that keratin, the main constituent of wool and of epidermis, is particularly susceptible to attack by sulphide, while the collagen of the skin is quite resistant. Now, there are three main chemicals which we can use to provide the sulphide in paint, these being sodium sulphide, sodium hydrosulphide, and calcium hydrosulphide. Let us consider what happens to each of these when it is dissolved in water and mixed with lime to form paint.

Sodium sulphide, as we know, breaks down when it is dissolved in water to form sodium hydrosulphide and caustic soda. When lime is added to this solution, a further change takes place. The lime reacts with the sodium hydrosulphide to form calcium hydrosulphide and a further quantity of caustic soda. The final result is, therefore, calcium hydrosulphide plus two lots of caustic soda.

Sodium hydrosulphide does not undergo any change when it is dissolved in water, but when mixed with lime, forms calcium hydrosulphide and caustic soda. It therefore ends up as calcium hydrosulphide plus one lot of caustic soda.

Calcium hydrosulphide is not changed at all, either when it is dissolved in water or when lime is added to it.

So, no matter which of the three chemicals we use, we end up with a paint containing its sulphide in the form of calcium hydrosulphide. The amount and kind of alkali present is, however, quite different in the three cases. Paint made with sodium sulphide contains as alkali the lime and a very considerable amount of caustic soda formed from the sodium sulphide. Although lime is a relatively mild alkali, largely because of its low solubility, caustic soda is a very strong one, and has, as you know, a very marked plumping action on the pelt. Sodium hydrosulphide paint contains only about half as much caustic soda as sulphide paint, and is therefore less strongly alkaline. Finally, calcium hydrosulphide paint has only the alkalinity of the lime it contains. It is thus the least alkaline and the least plumping of the three. The effect of the plumping action we shall leave until a little later, but the alkalinity of the paint affects its dewoolling properties, and we shall discuss this aspect of the matter now.

We should mention in passing that the chemist would not be very happy about the explanation given above of what happens when paint is made up. He would prefer to talk in terms of "sodium ions", "calcium ions", and "hydroxyl ions" because, of course, all the chemicals in the paint ionise in solution. Although his explanation would be more scientifically accurate, it would be much more difficult to understand unless you had studied a good deal of chemistry, and it would come to much the same thing in the long run.

The Action of the Alkali in Paint

Sulphide will attack wool only in alkaline conditions. If the pH is below 9, it has very little effect. As the pH is increased above 9, the rate of attack increases rapidly up to a pH of about 12·5. Raising the pH above 12·5 does not increase the rate of attack very much. Now, a saturated solution of lime has a pH of 12·5, so it would appear that paint containing lime would be alkaline enough for the sulphide to do its work. But it must be borne in mind that the pH has to be 12·5 *at the wool roots*. As the paint soaks its way through from the flesh side of the skin, its alkali is being constantly absorbed and neutralised by the skin proteins. To replace this lost alkali, more lime has to dissolve from the paint and gradually work its way through towards the wool roots. This process must continue until finally the skin proteins have absorbed all the alkali they can neutralise. Only then can the pH at the wool roots rise as high as that of the lime. But as the skin proteins become alkaline they absorb water and swell. There is not sufficient water in the paint for them to swell to the extent shown in fig. 2, but they swell as much as they can with the water available. The water left to dissolve lime is therefore very limited. Since lime is not very soluble, and since, even when it is in solution, it moves through the skin comparatively slowly – much more slowly than caustic soda does – a paint containing no caustic soda takes a considerable time to establish alkaline conditions at the wool roots. In other words, caustic soda makes paint much more penetrating. For this reason, paint made with calcium hydrosulphide works well only with skins which are thin and open, and through which the lime can penetrate easily. Sodium hydrosulphide paint, which contains a proportion of the stronger and faster-moving caustic soda, is more effective than calcium hydrosulphide. Except when used on particularly thick and tough skins, it gives satisfactory pulling. Sodium sulphide paint is, of course, more strongly alkaline and more quickly penetrating than either of the other two. It can cope more effectively with the meat and fat which are all too frequently found on the flesh side of the skin. With the advent of pre-paint fleshing, the necessity for its use should be greatly decreased.

If it were merely a matter of loosening the wool, sodium sulphide paint would be the best and most reliable to use. But the fellmonger is concerned with the pelt as well. Although collagen is resistant to sulphide, it is attacked by alkalis, and especially by strong ones such as caustic soda. The more caustic soda the pelt contains, the greater the risk of pelt damage, and the more rapidly the pelt will plump when it is put into the lime dolly and given the water it needs to do so. If we want to turn out good pelts, we must keep the caustic soda in the paint to a minimum. This is, of course, the basis of the age-old argument between the wool-pullers who want the wool to be loose on the skins, and the pelt man who wants the paint strength kept down. To some extent, the answer must be a compromise between the two conflicting views, but it is possible to do something about the excessive alkalinity of sulphide paint without unduly reducing its wool-loosening powers.

One method of reducing the alkalinity of sodium sulphide paint is by the addition of calcium chloride. This method has been used to some extent in New Zealand, but has never become very popular. Calcium chloride reacts with caustic soda to form lime and sodium chloride (common salt), so that, by adding varying amounts of calcium chloride, it is possible to reduce the caustic soda in the paint to any desired degree. In fact, it is possible to remove it altogether and to obtain what is in effect a calcium hydrosulphide paint. Now that sodium hydrosulphide is available in New Zealand, however, a simpler and less expensive method of accomplishing the same result is possible. By mixing sodium hydrosulphide and sodium sulphide in varying proportions, any desired degree of caustic soda alkalinity can be obtained, from that of a straight sodium hydrosulphide to that of a straight sulphide. Straight hydrosulphide can be used on skins which pull easily, and straight sulphide where pulling is particularly difficult. Mixtures of the two can be used in intermediate cases. It is thus possible to reduce the alkalinity of a paint without altering its sulphide content.

Lime as a Source of Alkali

So far we have neglected the contribution which the lime makes to the alkalinity of the paint – and a most important contribution it is. If we had to depend entirely on a strong alkali like caustic soda to make the skin alkaline, we would be up against a very serious difficulty. It takes quite a considerable amount of alkali to satisfy the neutralising power of the skin proteins. If we were to put the full amount of caustic soda into the paint, we would have a very concentrated solution of caustic soda in contact with the flesh side of the skin and, long before the caustic soda could soak through and be neutralised by the skin proteins, it would have severely damaged the flesh side of the pelt. Our only method of working would be to put only a small portion of the caustic soda in the paint, wait until this had been neutralised by the skin, add a little more, and so on until we had added the whole amount. Such a procedure would be quite impossible in practice, of course, but by using lime we can obtain just the same result quite automatically. Lime is not very soluble and is a milder alkali than caustic soda in any case. No matter how much lime is present, it can never produce such a high alkalinity that there is risk of pelt damage. So we can quite safely make up a paint containing a large excess of lime. As the paint soaks into the skin and its alkalinity is neutralised by the skin proteins, more lime dissolves from the paint to replace the lost alkali, and so the process goes on until the whole skin becomes alkaline. The lime in the paint acts as a reservoir of alkali which maintains a moderate alkalinity in the skin. It provides the main bulk of the alkali required by the skin and, in most cases, needs only a slight boost from a small amount of the stronger and more penetrating caustic soda.

Valuable as lime is as an alkalinity regulator in the skin, it has serious disadvantages as far as the wool is concerned, since it is particularly difficult to scour out. Wool contaminated with lime brings a considerably lower price than wool which is free from lime and, under modern freezing-works conditions, it is inevitable that a proportion of the wool will become contaminated. In order to overcome this trouble with their valuable Merino wool, the Australians tried to devise a paint which did not contain any lime at all. They used as a thickener a type of fuller's earth which is quite neutral in reaction, and they therefore had to face the problem of making the skins alkaline by some other means. Caustic soda was far too drastic, and even the milder sodium carbonate (soda ash) was far too strong to incorporate in the paint. In the end, they had to resort to the expedient of soaking the skins in a 2 per cent solution of sodium carbonate for one to two hours before painting them with a sodium sulphide - fuller's earth paint. In this way, they were able to supply the skin with a relatively large amount of alkali in such a dilute form that the pelts were not damaged, but the method is so cumbersome and requires such large soaking tanks that it would be quite impractical in a freezing works. In spite of its disadvantages, lime is very hard to replace as a source of alkali in a depilatory paint.

Thickeners for Paint

If we were to mix a paint with only sufficient lime to act as a source of alkali for the skin, we would require only about 1 lb of lime for every gallon of sulphide solution, or about one-quarter of the lime usually incorporated in a paint. Such a mixture would, of course, be far too thin to use, and it is therefore necessary to thicken a depilatory paint in one manner or another. The most common method of thickening paint is simply to go on adding lime until the mixture is thick enough. In such a paint, three-quarters of the lime is merely there as a thickener and serves no purpose at all in dewoolling the skin. This excess lime is still there on the surface of the skin at the time of pulling, and it still holds, like a sponge, a certain amount of sulphide solution which has never been allowed to soak into the skin. In addition to holding back some sulphide, this large amount of excess lime tends to contaminate the wool during the handling of the skins or via the barrows and the pullers' beams. All this trouble occurs because it takes such a large quantity of lime to thicken quite a small volume of paint. In other words, lime is not a very efficient thickener.

Various other thickeners have been tried, both on a laboratory scale and in the fellmongery, but none of them have had wide acceptance. Kaolin or china clay is not a desirable thickener because it absorbs the sulphide to an even greater extent than lime does, and will not release it to the skin. Flour has been used commercially to some extent, but has never become very popular. In the presence of caustic soda, it takes only about 1½ lb of flour to thicken 10 gallons of paint, whereas it takes about 30 lb of lime to achieve the same result. The film of flour paint collapses as the lime and sulphide are absorbed by the skin, leaving only a very thin layer on the flesh side by the time the skin is ready for pulling. There is thus very little hold-up of sulphide, and very little solid matter to get on to the wool. However, because of the difficulty of incorporating it into the paint and for various other reasons, flour is not widely used. For all its disadvantages, lime is still the most popular thickener.

Synthetic Detergents

Synthetic detergents, when they were introduced, seemed to offer the possibility of improving the penetrating power of paint, especially where fat was present. In actual practice, however, they proved a disappointment, and their incorporation in paint made little difference to it.

Control of Paint Strength

Whatever the constituents used, it is imperative for the sake of the pelts that the paint be kept to the lowest strength which will give good pulling. It is quite easy to test the strength of the sulphide solution with a hydrometer and to keep it within reasonable limits, but this is only half the story. What really matters is the amount of sulphide applied per square inch of skin. Within limits, a weaker paint applied more heavily will have the same effect as a stronger paint applied more lightly. The "strength" of the paint, as the fellmonger uses the term, means very little unless he also specifies the number of skins painted per gallon. The figure that really means something is the weight of sodium sulphide used per 1,000 skins.

Uniform painting is more easily achieved if the paint itself is kept to a uniform consistency. The thickness of paint can be tested with a hydrometer, but this is a little tricky. The hydrometer settles very slowly in paint, but if you "help" it down, you may push it in too far, get paint on the spindle, and thus make it read too low. Used carefully, however, the hydrometer is quite a useful guide. Another and probably more reliable method of testing the consistency of paint is to use a funnel with a fairly small outlet. The funnel is filled with a satisfactory paint, and a stopwatch is used to measure the time for the paint to run out of the funnel. A paint which runs out more quickly than the standard requires more thickener. The main point to watch is that the paint must be free from lumps which would block the outlet.

Other Factors Which Affect Depilation

(a) *Type of Skin.* The type of skin, whether milk lamb or sheep, whether shorn or long-woolled, makes a big difference to the strength of the paint necessary to loosen the wool. Experience is the best guide in allowing for this factor.

(b) *Moisture.* It is generally agreed that skins which have been wrung too dry prior to painting are difficult to pull. This is probably because water is necessary to carry the sulphide and alkali through to the wool roots. But a wet skin means wet wool, and therein lies a danger. With mass-production methods such as are used in our freezing-works fellmongeries, it is necessary to use paint of such a strength that the toughest and thickest skins of the day will pull satisfactorily. This means inevitably that the thinner and more open skins will get paint that is too strong for them and that, long before they are pulled, quite a large quantity of sulphide will have soaked through and on to the grain surface. If the wool is wet, this sulphide will be carried up the wool fibres, causing damage as it goes. In some cases, a good ¼ in. of the wool staple above skin level will be severely damaged. You can test this for yourself by applying to the wool a solution of sodium nitroprusside which turns pink immediately if sulphide is present.

(c) *Temperature.* Temperature is another factor which influences the effect of paint on a skin. At a higher temperature, not only is the wool more readily attacked by the sulphide, but the collagen of the skin is also damaged more easily by the alkali of the paint. You will all have observed that a cold night makes pulling harder, and some at least of you will have seen the effect of overheating on a pile of painted skins. The action of sulphide on the wool roots and the growth of bacteria in the wool both generate heat, and, as you all know, the temperature in the centre of a stack of painted skins can be several degrees higher than that of the air in the cellar. Now, as the temperature in the stack rises, the rate of action of the sulphide increases, the bacteria in the wool grow more quickly, and heat is generated still more rapidly. Unless the extra heat can get away, the temperature can soon rise to dangerous heights. It is for this reason that, in hot weather, stacks of painted skins are kept small. Of course, the problem is not so great in those fellmongeries where the skins are doubled over and hung on racks or conveyor chains. With each skin hung individually, the heat has a better chance of escaping, but even so, with long-woolled skins hung close together, there is a danger of the air circulation being so hindered that the temperature may rise unduly. On the other hand, if excessive ventilation is provided to get rid of the heat, there is danger of individually hung skins drying out and being affected by lime blast. The ideal is undoubtedly an air-conditioned cellar provided with good air circulation, in which the skins are hung individually. Such a cellar could be kept at a steady temperature and a high humidity which would prevent the skins from drying out.

(d) *Meat and Fat.* One of the greatest obstacles to efficient dewoolling of sheepskins is the presence of fat and meat on the flesh side of the skin. Paint cannot penetrate such tissue, and even sulphide paint with its greater penetration can work in under a lump of fat to a distance of only about one-tenth of an inch. For all practical purposes, the whole area above a piece of fat or meat will refuse to pull. Even where the shears are used carefully on such areas, the loss of wool is very considerable. Not only that, but the extra sulphide used in the paint and in the lime dolly to shift the wool means that there is too much caustic soda present for the good of the pelts. The introduction of pre-paint fleshers, of which there are two models now available, should do a great deal to solve this problem. The removal of the lumps of fat and meat should do away with the woolly patches which have to be dealt with by means of shears and lime dolly. The removal or breaking up of the thin film of fat with its accompanying membrane which is so often present on the flesh side should allow of a decrease in the strength of the paint necessary for good pulling, and should permit of the more widespread use of hydrosulphide with its lesser alkalinity.

(e) *Time for Depilation.* In New Zealand the paint strength is so adjusted that the skins are ready to pull in 24 hours. This is, of course, to fit in with the working day, and there would be little point in attempting to speed up the wool loosening unless the time could be reduced to one to two hours, thus enabling skins to be pulled on the day they were painted. No known depilatory will act as quickly as that.

(f) *Method of Paint Application.* The time-honoured method of hand-painting with brushes is gradually being replaced by spray-painting which is completely automatic. It has been recognised for a long time that the backbone area and the neck and butt, where the skin is thick and dense, require stronger paint than do the flanks where the skin is much thinner. Even when the one strength of paint is used for the whole skin, a good hand-painter will put more paint on the thicker areas of the skin to increase the depilatory action there. The same effect is achieved in many fellmongeries by using a stronger paint on the backs, necks, and butts, and a weaker one on the flanks. The same two methods are used in spray-painting. Some systems use three separate sprays arranged across the width of the paint table, the middle spray being supplied with stronger paint than the two outer ones which cover the flanks. In other systems, only one spray is used, but the nozzle is designed to put about one and a half times as much paint on the backs as it does on the flanks. With sprays of this type, it is essential to check the paint distribution at frequent intervals. Paint, containing as it does large quantities of solid lime particles, has a very abrasive action on metal, and does not take long to produce wear in the nozzle. A very small amount of wear in the nozzle can alter the pattern of the paint distribution very considerably, and it is not at all uncommon for a worn or badly designed nozzle to put more paint on the flanks than on the backs. The ideal distribution is of the type shown in fig. 3, although minor variations from it will be found in practice and are of little importance because the paint will even out to some extent when the skins are stacked or folded. Figs. 4 and 5 show distributions actually found in commercial spray-painting. The nozzle in fig. 4 is producing a very good pattern. That in fig. 5 needs replacing, although small lambskins placed centrally on the belt may miss the heavy paint on the edges. Larger skins will almost certainly have "glassy" flanks when pulled.

Taking an overall view, the painting process, although the best method of depilation we have at our disposal, is very far from being perfect. Wool is lost by the destruction of the wool roots and varying amounts of the wool staple. To this lost wool must

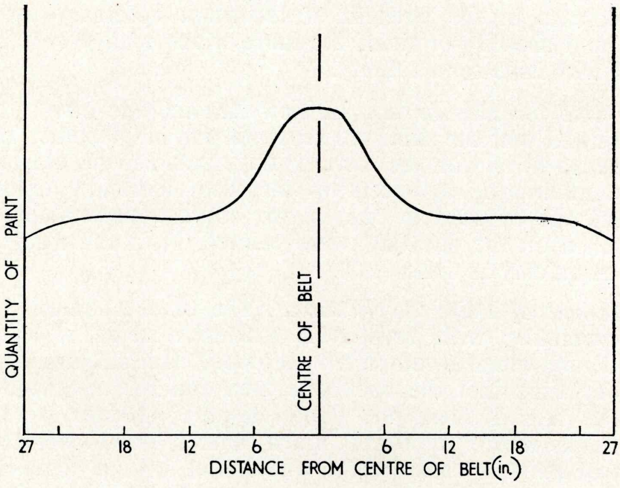


FIG. 3.

be added that left on the pelt after pulling. And, finally, there is the loss of value in the wool contaminated with paint at the edges of the skin or by contact with paint-smeared surfaces such as pullers' beams and gloves. At a conservative estimate, at least 10 per cent of the full value of the wool on the skins must be lost each year, and this is no inconsiderable loss.

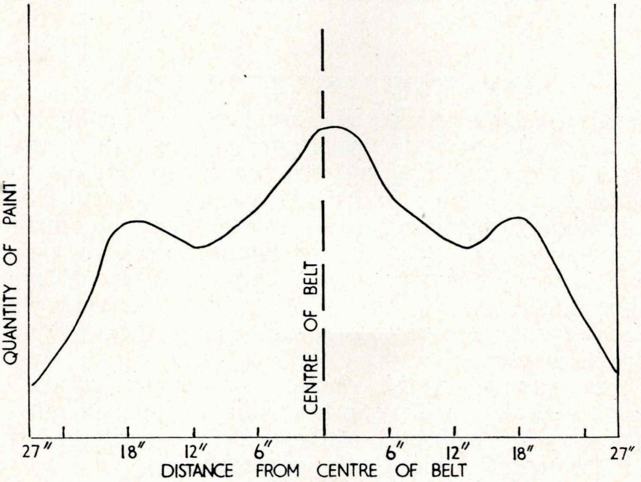


FIG. 4.

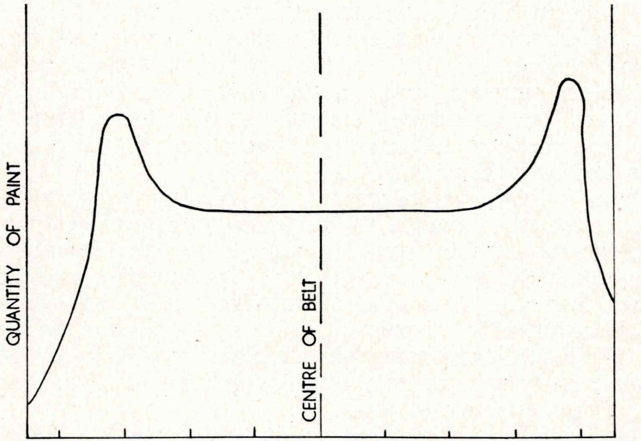


FIG. 5.

DEPILATION LOAD

In connection with trials of various depilatories, you may have come across the term "depilation load". This is a laboratory test measuring the degree of wool loosening, and is the force necessary to pull out a certain quantity of wool under rigidly specified conditions. The higher the depilation load, the more difficult the pulling. For "commercial pulling" as we know it in New Zealand, the depilation load has to be less than 1.

LIME - SODIUM-SULPHIDE LIMING

In modern fellmongery practice in this country, liming invariably means the treatment of the pelts after pulling with a liquor containing an excess of lime and sharpened with sodium sulphide. This treatment, at least in its early stages, is carried out in a dolly. Although there are some variations in the methods of working in the later stages of the liming process as carried out in New Zealand fellmongeries, the basic principles of liming are the same in all cases. In the main part of the discussion we can therefore ignore these variations and refer to them briefly at the end of the chapter.

At the beginning of this chapter, we enumerated the objects which we wished to achieve in the liming process. We are now in a position to deal with each of them in some detail, and we shall do so in the order in which they appear earlier.

Removal of Wool

We have already dealt fairly fully with the removal of wool from the skin, but, even under the most favourable conditions and with the most conscientious pullers, the pelt will still carry a certain amount of wool when it reaches the lime dolly. Unless this wool is removed during liming, it will persist right through the rest of the processing and will become firmly fixed in the pelt during pickling, to be viewed with strong disapproval by the tanner who buys the pelts.

Sodium sulphide is, of course, the obvious agent to use for removing the wool, and in the lime dolly where the sulphide can attack the wool roots from the grain side, the loosening effect is comparatively rapid, even though the sulphide concentration is much less than it is in depilatory paint. The rubbing of the pelts one against the other in the dolly soon dislodges the loosened wool. The wool fibres themselves are also attacked by the sulphide and are usually reduced to a mushy condition which makes them useless as a commercial product.

In connection with the destruction of wool in the lime dolly, there is a phenomenon, known as "immunisation", of which you may have heard. If a hide or calfskin is put into a straight lime liquor and left there for some time before the sulphide is added, the hair is most difficult to remove, even although quite large quantities of sulphide are added subsequently. The alkali has immunised the hair to attack by the sulphide. This action does not occur if the sulphide is added to the liquor before the hides are put in, and since, in the fellmongery, the pelts bring their own sulphide with them into the lime liquor, one would think that the trouble would not occur with sheep pelts. It does seem to take place, however, and gives rise to those troublesome patches of wool which persist in the lime dolly and right through to the pickled pelt. The only reasonable explanation seems to be that where there is fat or meat on the flesh side of the skin, the fast-moving caustic soda from the paint works in from round the sides and immunises the wool roots before the slower-moving sulphide can get there.

For the destruction and removal of wool, a high concentration of sodium sulphide is an obvious advantage but, once again, pelt quality demands that the concentration be kept low. The wool must certainly be removed, but any sulphide, with its accompanying caustic soda alkalinity, over and above the barest minimum which will achieve this object, will almost certainly result in a pelt of inferior quality. In some fellmongeries it is the practice to use a somewhat higher concentration of sulphide for the first half-hour or so of liming and to reduce this as soon as the wool is moving freely. It is certainly better to do this than to leave the concentration high throughout the whole of the liming period. When pelts are to be left in the lime dolly for more than 24 hours, for example, over a weekend, the sulphide concentration in the dolly must be reduced to a lower figure than normal if pelt quality is to be maintained. This lower concentration of sulphide would be insufficient to loosen the wool, and the procedure outlined in this paragraph is the only one likely to give satisfactory results.

Removal of Epidermis

The epidermis or "scud" will, if the paint has not been too strong, still remain on the pelt. Scud adhering to the wool is normally a sign of strong paint. Since the scud, like the wool, consists mainly of keratin, it too is softened and loosened by the action of the sulphide and is rubbed off by the movement of the pelts against each other in the lime dolly. The removal of the epidermis is similar in every way to the removal of the wool.

Opening Up of the Fibre Structure

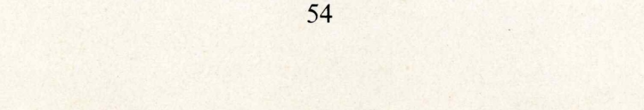
Coming now to the effect of liming on the pelt itself, the first action is to swell and plump the fibres and to open up the fibre structure. If you look again at fig. 2, you will see that collagen absorbs water and swells both in alkaline and in acid solutions.

Now, the pelt as it comes from the pullers, is heavily charged with both lime and sodium sulphide derived from the paint and is, of course, highly alkaline. The pH is well over 12, and you will see from fig. 2 that even at pH 12 collagen is capable of absorbing quite large amounts of water. The only reason why a painted skin is not greatly swollen is that there has not been enough water in the paint for it to absorb. A painted skin is therefore a "thirsty" skin, eagerly waiting to absorb any water it can get hold of. And, in the lime dolly, there is water to spare. The moment the pelt is put into the lime liquor, it starts to swell. This swelling is just what we require, but (and the "but" is a big and important one) the degree, and above all, the rapidity of the swelling must be very carefully controlled indeed, if "mottle" and "loose grain" are to be kept at bay.

The reason for this is not hard to understand. The rate and degree of swelling are not the same in the grain layer as in the flesh layer. If you care to go to the trouble, you can prove this for yourself. Take a piece of unlimed pelt and carefully trace its outline on a piece of paper. Split the pelt with a razor blade into its two layers and then lime both layers separately. You will find, of course, that both layers will swell and become thicker, but you will also find that, whereas the grain layer will expand and occupy a greater area than it did originally, the area of the flesh layer will stay about the same as it was before it was limed.

In an ordinary unsplit pelt the same tendency exists, but because the two layers are joined together the grain layer is restrained by the flesh layer and cannot expand freely. Provided that the swelling action is slow and not too drastic, the pelt can adjust itself to the strains produced by the grain layer trying to pull away from the flesh layer, and any distortion which may occur is of a temporary nature and disappears during deliming. When the swelling is rapid, however, the pelt cannot adjust itself to the strains, and the grain layer must wrinkle or mottle itself over the flesh layer to accommodate its increased area. In extreme cases, and especially in those pelts where the junction between the two layers is weak, the grain layer may even split away from the flesh layer over quite a large area, giving rise to what is known as "loose grain". The diagram will help to make clear what happens in this case.

The strains indicated by the arrows in I produce the result shown in II.



The "mottle" or "loose grain" produced by over-rapid swelling involves permanent damage to the weave of the pelt and will not disappear on deliming. Owing to the nature of the skin in the neck region, this type of damage is more likely to occur there than in other parts of the pelt. The difference between slow and rapid swelling of a pelt can be appreciated if you think of what happens when you blow up a toy balloon. Blow it up rapidly, and it will burst at a weak spot. Blow it up slowly so that the strains can even themselves out, and it can be inflated safely to a large size. The action of lime liquor on a pelt is very similar to this.

Having seen why it is necessary to swell or plump a pelt gradually and gently in the lime dolly, let us now consider how best this can be accomplished in practice. Perhaps the easiest way of doing so will be to set out the factors which cause rapid swelling. If we know these, we can take steps to avoid them. The main causes of too rapid absorption of water by pelts are:

(a) *Excess Alkali in the Lime Dolly.* As we have seen, lime alone can produce only a mild alkalinity in the lime liquor, and this amount of alkalinity is very unlikely to do the pelts any harm. When we add sodium sulphide to the liquor, however, we are, in effect, adding caustic soda, and it is this extra caustic soda alkalinity which constitutes the danger. Caustic soda produces much more severe swelling than does lime, even if the alkalinity is the same in both cases. There are few chemicals as drastic as caustic soda in producing a rapid swelling of pelts. Now, caustic soda in a lime liquor is not wholly objectionable. In fact, it is the more intense action of the caustic soda which makes it possible to reduce the time of liming from the two to three days which a straight lime liquor requires. But the amount of caustic soda alkalinity present in the liquor must be very carefully controlled indeed.

The most common cause of an excess of caustic soda in the lime dolly is an excess of sodium sulphide in the paint which the pelts have brought in with them. Some fellmongers attempt to wash out the excess in the dolly, but this is quite ineffective, since the caustic soda will have already combined with the skin proteins. To wash out this combined caustic soda takes some little time, and in the meanwhile, the rapid swelling of the pelt will have already taken place. At a later stage, when the caustic soda has had time to distribute itself through the lime liquor, washing out can be used successfully to reduce its concentration, but it is no use trying to wash out the excess caustic soda to prevent too rapid swelling of the pelts in the early stages of liming. There is only one way to keep the caustic soda to a safe level in the lime dolly, and that is to keep the strength of the paint as low as possible. Strong paint, quite apart from the damage it may do to the pelts before they are pulled, is very dangerous in the lime dolly. There is every reason for the fellmonger to keep his paint strength down to a minimum at all times. Should the sodium sulphide be found, on testing, to be too low to loosen the wool in the lime dolly, it is an easy matter to add a little hydrosulphide, and no damage is being done to the pelts while the test is being carried out. There is no danger in having too little sulphide in the dolly in the early stages of liming, but there is a very real danger in having too much.

It takes quite a lot of judgment and experience to work your lime dollies so that at no time is the concentration of sulphide greater than is necessary to move the wool on the pelts. This is especially the case if you are using a mellow lime, the advantages of which are described a little later on. You have to leave just sufficient sulphide in the dolly from the previous batch of pelts so that, when it is added to the sulphide from the incoming batch, the concentration in the dolly is not too high, and is, if anything, a little too low. The amount of sulphide left by the previous batch will depend on the size of the previous batch, the length of time it was washed for, the efficiency of the paddling, and the amount of water used for washing out. To gauge the washing out correctly means having a thorough knowledge of the dolly – no two dollies are exactly alike – and the conditions at the time. Then, of course, the amount of sulphide brought in by the incoming batch will depend on the size of the batch and on the strength of the paint used. In spite of the many factors involved, a little experience and a regular testing of the lime dollies will soon put you on the right track. The main points to remember are that the paint strength should be kept down to a minimum at all times and that the sulphide concentration in the lime dolly in the early stages of liming should be just great enough to move the wool and should at no time be greater.

A knowledge of the characteristics of each dolly is just as important when breaking down the sulphide strength after the wool has been loosened. If you know the dimensions of the dolly, it is an easy matter to calculate how much liquor to run out and replace with water in order to reduce the sulphide strength by any desired amount. A dipstick marked in gallons is a big help.

Sodium hydrosulphide is a much safer sharpener to use in a lime liquor than is sodium sulphide, because it introduces only half as much caustic soda alkalinity. By its use, we can obtain wool-loosening power without raising the caustic soda alkalinity to a dangerous value. It could be used much more widely in New Zealand fellmongeries than it is.

The contribution which the lime makes to the alkalinity is more or less constant. As in the paint, it acts as a reservoir of alkalinity, the insoluble excess dissolving as required. The pelts bring with them a considerable quantity of lime from the paint, and many fellmongers are of the opinion that this is quite sufficient for the liming of the pelts. On the other hand, it is quite common practice to add extra lime to the dolly, and there are many arguments in favour of so doing. In the first place, lime dissolves fairly slowly, and the more lime there is present, the more rapidly any lime which has been used up will be replaced. Then, some of the paint lime will have combined with the carbon dioxide of the air to form calcium carbonate which is quite useless for liming pelts, and the amount of useful lime carried by the pelts may be considerably less than was originally present in the paint. Finally, the lime particles on the pelts tend to stick together and form small grains which do not dissolve as readily or rapidly as the fresh lime which is in a finely powdered form. In any case, the extra lime cannot possibly do any harm, and does not add to the alkalinity of the liquor.

The testing of the alkalinity of a lime liquor is not easy, but since the caustic soda is introduced as sodium sulphide, measuring the sulphide content of the liquor gives a very good indication of the caustic soda alkalinity present. And, as we have seen, it is the caustic soda which concerns us most. Fortunately, there is a fairly simple method of measuring the sulphide in a liquor, and most fellmongers these days control their lime dollies by means of the test which is described in Appendix 2. Of course, where sodium hydrosulphide has been used in the paint, the caustic soda alkalinity will be less for any given sulphide content than when sodium sulphide has been used.

To sum up the situation as regards alkalinity in the lime dolly, there are three simple and important rules to follow:

(1) Keep the strength of the paint down to the lowest possible figure which will give workable pulling;

(2) Test every lime dolly for sulphide, and keep the sulphide content of the dolly to the lowest possible figure which will loosen wool;

(3) As soon as the wool is moving freely, reduce the sulphide in the dolly to that concentration which you know from experience will give correct liming in 20 to 24 hours.

(b) *Paddling.* The more the pelts are agitated in the dolly, the greater the contact between them and the lime liquor and the more rapidly they will absorb water. Vigorous and continuous paddling will therefore cause rapid swelling of the pelts. There is another danger with rapid paddling which we may well call attention to here. Pelts in the limed state are swollen, tender, and under strain. They are therefore particularly susceptible to mechanical damage to the weave of the pelt and especially to the grain surface. Where such damage is occurring, it can easily be detected by rubbing ochre on the grain of the pickled pelt and then washing it off with pickle liquor. The pigment will adhere to any roughened areas. To prevent undue swelling and to protect the grain surface, the aim should be to use paddle speeds only just sufficient to keep the pelts moving, and to paddle only long enough to make sure that the liquor reaches all portions of all the pelts. After the initial period is over, only intermittent paddling for short intervals is necessary.

(c) *Mellow Lime Liquor*. Lime liquors which have been used before contain protein and other dissolved matter from previous batches of pelts and especially from the wool which has been decomposed. This dissolved matter acts as a buffer in preventing the too rapid absorption of water by the incoming batch of pelts. It holds on to the water, so to speak, and releases it to the pelts only slowly and reluctantly. Pelts limed in a mellow liquor will therefore plump less rapidly and to a lesser degree than those limed in a fresh liquor. The "mellowness" can be overdone, however, and it is not desirable to let the liquor build up to a heavy consistency. The usual fellmongery practice is to give the pelts a partial wash in the lime dolly after liming is completed and before transferring them to the bate dolly. The wash water dilutes the lime liquor, so that when the pelts are taken out, there remains in the dolly a weakened lime liquor for the reception of the next batch of pelts. With this method, the dolly can be used for quite a long period without being emptied out. The degree of washing out in the lime dolly is governed by the sulphide to be left for the next batch of pelts as mentioned in (a) above.

(d) *High Temperature*. Water absorption by pelts will take place more rapidly at high temperatures than at low ones. Elevated temperatures should therefore be avoided. Apart from its effect on the rate of swelling, a high temperature will accelerate the attack of alkali on the pelt substance and may cause serious damage. Pelts, whether in a dolly or in a stack, should be kept as cool as possible.

If the points discussed above are given close attention, such faults as mottle and loose grain should be reduced to a minimum.

Removal of Non-fibrous Substances

The mass of non-fibrous protein matter and mucous substances which surround the collagen fibres and fill the spaces between them must all be removed during fellmongering to allow access for the tan liquors during tanning. Liming is the first and most important step in this removal. All such substances differ from collagen in that they are much more readily attacked and rendered soluble by alkali than is collagen itself. In the lime dolly, therefore, this interfibrillary matter is decomposed and reduced to a soluble state. Much of it is removed during the liming process itself, and the remainder is washed out during deliming. But unless these substances are sufficiently broken down during liming, the subsequent fellmongering processes will be powerless to remove them completely. The key to clearing the pelt structure of all interfibrillary matter is therefore correct liming.

Destruction of Nerves, Glands, etc.

The various skin structures such as nerves, blood vessels, muscles, and glands, which are essential to the living skin, but which are not wanted in the finished leather must be broken down before tanning. These, too, are readily attacked by alkali, and it is the liming which is responsible for their destruction.

Destruction of Fat-cell Membranes

Skin, as will be seen from photomicrographs, contains innumerable globules of fat each encased in a tough film of membrane. This fat, or most of it, must be removed by the tanner, and the liming process makes his task a relatively easy one. The alkali of the lime liquor attacks the membrane walls of the fat cells, which, after the pelts have been held about six weeks in the pickled state, collapse. The fat can then be readily removed by paraffin degreasing in the tannery.

Swelling of Meat Tissue

The fatty and meaty tissue adhering to the flesh side of the pelt is also swollen by the lime liquor and, where fleshing out of lime is practised is more easily removed by the fleshing machine.

Rupturing of Binding Proteins

The garters and sheaths of fibrous protein which bind the fibres and fibre bundles of collagen together are weakened and ruptured by the lime liquor, thus giving rise to both splitting and separation in the fibre structure of the pelt. Provided that these actions are not carried too far, they produce an improvement in pelt quality. Overliming, however, gives rise to too great a degree of separation and splitting and weakens the pelt structure. A correctly limed pelt has an appearance which is readily recognised by an experienced fellmonger, but which is virtually impossible to describe in words. Photomicrographs of pelt structure give some help, but experience is the best guide as to whether pelts are correctly limed or not.

From the foregoing, it will be obvious that liming is the most important operation in the processing of pelts and that mistakes in liming are difficult, if not impossible, to remedy at a later stage. The use of sodium sulphide to hasten the liming process has reduced the margin of safety and has made it necessary to maintain the strictest control over the operation. In the old days, when liming was a leisurely operation extending over several days, and when the small numbers of pelts handled made it possible to examine them daily to see whether they were fully limed, conditions were not so exacting. In the modern fellmongery, where the process is, in most cases, completed in 24 hours and where

1,000 or even 2,000 pelts have all to be given identical treatment in spite of individual differences, liming is a much more tricky operation.

LIMING PRACTICE IN NEW ZEALAND

The older method, which is still used to some extent, is to lime stack. The pelts after pulling are limed in a dolly for two hours or so according to the dolly space available, and are then stacked for three to five days while the liming process is completed. This method has the advantage that dolly space is required for only about one-third or one-quarter of the day's production of pelts, so that a smaller capital outlay is involved, but the labour costs for handling the pelts are greater than for the 24-hour process. The main disadvantages of lime stacking, apart from the extra labour involved, are that conditions are not uniform throughout the stack, and that drying out at the edges can give rise to "lime blast". Then, there is always the danger that, owing to pressure of work or shortage of labour, pelts may at times be left too long in the stacks, with consequent overliming and loss of substance.

The newer dolly liming or 24-hour process, which was introduced in about 1930, has rapidly found favour in this country. In this process, the whole operation is carried out in a dolly, the liquor being sharpened with sodium sulphide to such a degree that the pelts are limed in 24 hours. Since the pelts must come out at the end of 24 hours to make room for the next day's pelts, there is always a danger that too much sulphide will be used in an attempt to ensure that the pelts are completely limed. When using this process, therefore, the fellmonger must be doubly careful to keep his sulphide content under strict control. He is always walking the tightrope of correct liming, with the pitfalls of overliming on one side and underliming on the other. In the 24-hour process the margin between them is narrow indeed. In spite of its dangers and the fact that dolly space must be provided for a full day's output of pelts, the 24-hour process has steadily gained in popularity.

Neither method of liming is fool-proof, and good results can be obtained only by unremitting care and attention.

FAULTS ASSOCIATED WITH DEPILATION AND LIMING

Mottle

Mottle is found mainly in the neck region of the pelt. It consists of raised portions, usually in the shape of ridges or roughly square areas. The distortion of the pelt is permanent and is due to too rapid plumping in the lime dolly. The grain layer has buckled up over the flesh layer in those areas where the two layers are least firmly attached.

Loose Grain

This is a separation of the grain and flesh layers, again due to too rapid swelling. In this case, the strain has been so great that the expanding grain layer has broken away completely from the flesh layer. Loose grain may also be due to the type of skin which has an excessive fat layer between the grain and the flesh. In this case, the two layers may become separated during flaying or during liming, even when the greatest care is exercised. Pelts with loose grain can be used by the tanner for "splitters".

Leopard Grain

Leopard grain is damage to the surface of the grain layer with loss of "enamel". It is always associated with mottle, the main cause being mechanical damage to the raised portions of a mottled pelt by excessive paddling in the lime dolly. The chemical effect of excessive sodium sulphide or of holding for too long a period in the lime stack may also be a factor.

Lime Blast

When a painted or limed pelt dries out, the calcium carbonate formed by the action of the carbon dioxide in the air on the lime in the pelt is deposited in the structure of the pelt itself in the form of a harsh, sandpapery surface layer. This fault is found mainly in pelts which have been:

(a) Overwrung;
(b) Dried out at the edges during stacking either in the painted or limed condition, especially when exposed to air draughts; or
(c) Left too long after pulling before being put into the lime dolly.

Wool

Wool left on the pelts is a bad fault from the buyer's point of view.

MICROSTRUCTURE OF LIMED PELTS

Photomicrographs are given at the end of this book. Examine them carefully and compare them with photomicrographs of your own pelts. This will help you, with your own experience, to judge whether your liming procedure has been correct.

Chapter 4

DELIMING AND BATING

At the end of the liming process the pelt is swollen with absorbed water and contains large amounts of lime, both free and combined. By "free lime" we mean the lime dissolved in the water held by the pelt and also that held by the flesh in the form of particles, while "combined lime" is that in actual chemical combination with the pelt protein and with the partially decomposed interfibrillary matter. Free lime can be removed from the pelt by washing, but this would be a long and uneconomic process. Combined lime can be removed only by the use of deliming agents. Due to the presence of the lime, the pelt is very alkaline, having a pH of about 12·5.

Deliming and bating, the next steps in the processing of the pelts, are really two separate operations, although they are usually carried out in one dolly and often overlap each other. But it will be simpler if we discuss them separately.

DELIMING

The objects of deliming may be summarised as follows:

(i) To remove the majority of the lime, both free and combined, from the pelt. This automatically reduces the pH which, in turn, causes the swollen pelt to fall.

(ii) To remove the unwanted interfibrillary matter which has been decomposed by the lime liquor.

The first step in the removal of the lime is to wash the pelts with water, since water is the cheapest delimer of all. Now, although the limed pelts are swollen with water, they are capable of absorbing still more water. As we mentioned earlier, lime liquor contains dissolved protein matter which has a restraining influence on water absorption by the pelts and prevents them swelling to their fullest extent. So, if the limed pelts are put into clean water which contains none of these restraining substances, they will rapidly absorb further quantities. The mottle and loose grain which we have been so careful to avoid during liming, could quite easily appear at this stage if the washing were done by transferring the pelts into clean water. The trouble can be avoided in one of two ways. The pelts can be given only a brief surface wash in the lime dolly where the presence of the restraining substances prevents undue swelling, and can then be transferred to the bate dolly containing deliming salts. This method uses more delimer than does the other method, since much of the lime which could be washed out has to be neutralised by the delimer, but it avoids prolonged paddling of the pelts in the swollen and tender condition, which, as we saw in Chapter 3, can easily cause mechanical damage. The second method, which is widely practised in New Zealand fellmongeries, is to run water into the lime dolly before the pelts are removed, and in this way to give them a more thorough washing. With this method, the pelts are washed in a lime liquor of gradually decreasing strength, and all the changes to which the pelts are subjected are gradual ones. The danger of producing mottle is not very great, but the longer paddling of the swollen pelts is not particularly desirable. In spite of the increased cost of delimer, the first method is the better one.

Even if washing were continued for a very long time, only about 60 per cent of the lime in the pelt would be removed, and this would be only the free lime. Such a procedure would be quite impractical. To remove the remainder of the lime in a reasonable time, we must therefore resort to chemical means. The most obvious method of removing an alkali like lime is to use an acid which will convert it into a soluble salt which can then be washed out. Hydrochloric acid would be ideal for the purpose, since the calcium chloride which would be formed is very soluble in water and would wash out very readily. But, apart from the cost of hydrochloric acid in New Zealand, there is a serious disadvantage in its use. If any considerable amount of acid were added in one dose, it would take some little time to soak into the pelts and be neutralised by the lime they contain. In the meantime, there would be an excess of acid in the liquor and, if this were too great, it could easily damage the surface of the pelts. If acid were used to delime pelts, it would therefore have to be added slowly and in small doses. After each addition, time would have to be allowed for this acid to be neutralised before the next addition. Towards the end of deliming, the additions would have to be smaller as the quantity of lime left grew less, and the time allowed between additions would have to be longer as the acid had to travel further in towards the middle of the pelt to find lime to neutralise. At all times, care would have to be taken that the concentration of acid in the liquor did not rise high enough to constitute a danger to the pelts. It is doubtful whether, even with experience, a fixed routine for the addition of acid could be worked out, because variations in the pelts, in the liming, and in the washing out after liming would all affect the quantity of acid required. Other acids, less dangerous to the pelts, could be used in place of hydrochloric, but most of them are ruled out on the score of expense. Sulphuric acid, which is relatively cheap, would have to be handled just as carefully as hydrochloric, and has the additional disadvantage that the calcium sulphate which is formed when sulphuric acid neutralises lime is not very soluble and is rather difficult to wash out of the pelt. Deliming with acid, usually hydrochloric, is practised to quite a considerable extent overseas, but the low cost of the acid there, the smaller scale of operations, and the permanent skilled staff make conditions much more favourable. Attempts have been made to use acid in New Zealand, but they have been abandoned in favour of deliming with sal ammoniac or ammonium sulphate, which we shall discuss next.

Sal ammoniac (the chemist calls it ammonium chloride) and ammonium sulphate are two salts of ammonia which have the power of neutralising lime, but which can never produce strongly acid conditions in the dolly. They act as if they were very weak acids instead of salts. The way in which they neutralise lime may be represented as follows:

ammonium chloride + lime = calcium chloride + ammonia
ammonium sulphate + lime = calcium sulphate + ammonia

You will have noticed that a bate dolly smells strongly of ammonia when deliming is in progress, especially when it is warm. It may occur to you that ammonium sulphate should not be a good delimer because it forms the insoluble calcium sulphate. But calcium sulphate is quite soluble in solutions containing ammonium salts and, in these circumstances, ammonium sulphate is an efficient delimer. It is used, in fact, to an increasing extent in proprietary bates. Neither sal ammoniac nor ammonium sulphate can reduce the pH of the liquor below about 5·5, which is only slightly on the acid side and could not possibly harm the pelts. Under deliming conditions the presence of ammonia keeps the pH very much higher than this and, in actual practice, it is quite difficult to get the pH down even as low as 8·5 or 9. This means that an excess of either of these two salts is perfectly harmless. It is thus possible to add the whole of the sal ammoniac to the dolly in one dose, to be drawn on gradually by the pelts as the lime is neutralised. The use of sal ammoniac or ammonium sulphate thus entails the minimum of supervision and makes the deliming process more or less foolproof. Under New Zealand conditions, the method has such obvious advantages that its popularity is not difficult to understand.

Until the majority of the lime in the pelts has been neutralised, paddling should be gentle and the temperature should be kept low. High temperatures and vigorous paddling while the pelts are still in a swollen condition will damage the pelts in the same way as in the lime dolly. The damage will be particularly marked in the grain layer.

Once the bulk of the lime in the pelts has been neutralised and the pelts have fallen, however, warm water can be used safely and, in fact, its use is necessary for the complete removal of the unwanted, decomposed protein matter. This interfibrillary material cannot be washed out easily with cold water, but is fairly readily removed by warm water. If the pelts are to be bated, the temperature is raised in the last stages of deliming. If not, the pelts are washed with warm water after deliming. But, in both cases, care must be exercised in the manner in which the dolly is heated. To raise the temperature in the dolly quickly, fairly hot water must be admitted, and should this strike the pelts directly as they circulate, local areas of "blast" or "burning" will be produced. Baffles over the water inlets will help, but even with these the temperature of the incoming water should be kept as low as possible and should preferably be thermostatically controlled. The same precautions must be taken with those systems in which the liquor is circulated through an external heater. It is much better to heat a dolly slowly than to risk damaging the pelts.

If the pelts are not to be bated, a warm-water wash followed by a thorough cold-water washing will complete the process. The calcium salts formed by the delimer, as well as the decomposed protein matter and the mucins, will all be washed out. The pelts will then be ready for pickling.

BATING

The objects of bating are:

(i) To give the pelts a smooth, silky feel;
(ii) To open up the structure of the pelts more fully;
(iii) To give softness, fullness, and suppleness to the pelts.

If the pelts are to be bated, there are two alternative procedures which can be followed after the liming process is completed. One method is to wash the pelts and then to carry out a partial deliming with sal ammoniac in the manner outlined above. In the latter stages of deliming, the temperature is raised and the bate added. The other method is to add the bate immediately the washing of the limed pelts is completed and to rely on the ammonium salts in the bate for deliming. As you know, all commercial bates contain a large proportion of either sal ammoniac or ammonium sulphate, and are therefore both delimers and bates. Some fellmongers follow the second procedure, but add some additional delimer.

The tanner can bate to varying degrees according to the purpose for which the finished leather is required, but the fellmonger, who seldom knows what his pelts will be used for, can only aim at a moderate degree of bating which will be suitable for most purposes.

The practice of bating is a very old one in tannery procedure, and animal excrement was originally used for the purpose. Strictly speaking, "bating" refers only to the use of hen or pigeon manure. When dog dung was used, the process was known as "puering". Liquors were kept for a considerable time and were merely strengthened from time to time by the addition of more dung with each succeeding pack of skins. Needless to say, the bate shop was the filthiest and most disgusting section of the tannery. But before anything could be done to improve matters, it was necessary to find out exactly what it was in the dung infusions which brought about the desirable changes in the pelts.

It was the work of J. T. Wood at the end of last century which showed that the active substances in animal excrement were the proteolytic enzymes which it contained. Enzymes were explained briefly in Chapter 2, and you will remember that proteolytic enzymes are those which aid in the decomposition of proteins. As we mentioned in Chapter 2, the particular enzyme which is concerned in bating is trypsin, but as a matter of fact, commercial bates contain one or more of a group of enzymes closely related to trypsin, and usually known for convenience as "tryptic enzymes". These differ from most other proteolytic enzymes in that they are most active in a slightly alkaline medium. They show their greatest activity in a pH range of 8–9, and in a temperature range of 90–100°F. Once the nature of the active substances had been established, the way was open to substitute for dung an enzyme preparation derived from other sources.

Commercial bates based on Wood's discovery have been on the market since the early part of this century. They all contain tryptic enzymes which are obtained in some cases from animal pancreas glands, and in some cases from moulds or bacteria. All these preparations consist of mixtures of enzymes, each with a slightly different action on proteins. Enzyme bates prepared by different firms, or prepared by the same firm from different raw materials, may differ somewhat from each other in the kinds and proportions of the various tryptic enzymes present. It is therefore quite possible that one brand of bate may give better results than another with a particular class of pelts or in conjunction with a particular liming process.

We have already noted that tryptic enzymes work best in the pH range 8–9, although some recent work suggests that even at pH 9·5 their bating power is very little impaired, if at all. But, until the deliming salts have neutralised the lime and reduced the pH to about 9, the bating enzymes cannot come into action. It is therefore most important, when using a bate, to ensure that the pH of the bate liquor is reduced adequately; otherwise an expensive bating material is being used for a job which could be done equally well by sal ammoniac at a fraction of the cost. When ammonium salts are used as delimers, it is by no means easy to get the pH down below 9, since the ammonia in the liquor tends to keep the pH up. Provided that sufficient sal ammoniac is used, however, and that time is allowed for it to act, the pH can be brought down sufficiently. Too little attention is paid to this point in New Zealand fellmongeries, and it is feared that a great deal of expensive enzyme bate is simply wasted. Test papers should be kept beside the bate dollies, and the pH of the bate liquors tested frequently. When acid deliming is practised, the pH can be brought down as low as desired; in fact, it is all too easy to bring the pH lower than is desirable or safe.

Temperature of bating is also important. The enzymes show little activity at ordinary temperatures, but, on the other hand, they are destroyed completely at temperatures near boiling. The bate enzymes work best at about 95–100°F, and their activity falls off rapidly at higher or lower temperatures. The warming of the bate liquor therefore serves two purposes:

(i) It aids in the removal of decomposed protein matter which has not already been washed out with cold water.

(ii) It provides suitable conditions for the action of the bate enzymes.

As has already been mentioned, commercial bates contain either sal ammoniac or ammonium sulphate as well as the enzyme itself. If one of these bates is used with pelts which have not been delimed, the deliming salts in the bate must do their part before the enzyme can act at all. The enzyme portion of the bate simply lies dormant until the pH and the temperature are right for it. When the pelts have been delimed with sal ammoniac and the temperature of the dolly raised before the bate is added, the enzyme comes into action with little delay.

The exact effect of the bating action on the pelt is still a matter for argument among scientists who have studied the problem. At present, it appears that the action is a complex one, and that it probably involves further decomposition of the interfibrillary protein matter which has already been attacked by the lime liquor. It may well be that, as has been put forward by other workers in this field, the enzyme digests pro-collagen and collagen which has already been attacked by the alkali in the lime dolly. In New Zealand fellmongery practice, where the time of bating is so short and when the pH of the bate liquor is often so unfavourable, the changes must be very slight indeed, and it is not surprising that these changes are so difficult to track down and identify. In fact, it is not surprising that there are those who hold the opinion that the short bating given in New Zealand fellmongeries is of doubtful value, and that simple deliming is all that is required. This criticism is levelled only at the short bating given by the fellmonger, of course. The longer bating given by the tanner produces real and valuable changes in the pelt.

But if the bating process is somewhat of a puzzle to the scientist, the practical results are obvious to the tanner. A pelt which has been properly and fully bated has a characteristic smooth, silky feel; it will retain the impression when pinched between finger and thumb; and it is sufficiently porous to allow air to be squeezed through it. These properties, which are not found in a pelt which has been merely delimed, must naturally be due to some changes in the pelt structure. Since we do not understand these changes fully, we must be satisfied in the meantime to use preparations capable of producing the effects which the fellmonger knows how to recognise and which the tanner's experience tells him will produce the kind of leather he requires. Above all, the fellmonger must ensure that the conditions in his bate dollies are such that bating actually does take place and that he is not simply using an expensive delimer.

Chapter 5

PICKLING AND STORAGE

The pickling of pelts is carried out mainly for the purpose of preserving them from the action of moulds and bacteria until they are required for further processing by the tanner. New Zealand pelts are sometimes held in storage for two years or more, so the protection given them must be thorough and efficient.

The growth of bacteria and moulds is inhibited in very alkaline or very acid conditions, and alkali is, in fact, more effective than acid in this regard. But, unfortunately, collagen is also sensitive to alkali and would be severely damaged if pelts were stored for any length of time in an alkaline condition. Thus, although acid is less efficient than alkali for controlling moulds especially, we are forced to use it for preserving pelts. Sulphuric acid is used for pickling, partly because it is cheap, but mainly because it is particularly effective. Most of the other acids have some disadvantage which makes them unsuitable for the purpose. We should mention here, however, that care must be taken not to use too much acid, otherwise the pelts will be damaged. Although collagen is more resistant to acid than to alkali, it is attacked by acid if the concentration is too high, especially at elevated temperatures. This point is an important one, and we shall return to it later in this chapter.

But acid, like alkali, causes pelts to swell. So, if pelts were pickled in acid only, they would be swollen and tender. Not only would they occupy a great deal of space, but they would be very susceptible to mechanical damage. By adding salt to the pickle liquor, however, we can reduce the swelling. The broken line in fig. 2 makes this point clear. With the addition of salt, the pelts become tougher and much more suitable for handling and storage. The salt also plays a part in preventing the growth of moulds and bacteria, in that it locks up part of the water in the pelts and makes it unavailable to the micro-organisms. But even the combination of salt and acid does not give 100 per cent protection from moulds, some varieties of which can tolerate relatively high concentrations of acid. One particularly resistant mould is *Alternaria tenuis* which grows on white pine. Care should be taken to inspect casks for this organism, and to reject any which are infected with it. It is easily recognised as a dark-green, almost black, mould which shows up clearly on the timber.

You may have seen in books on tanning, references to the pickling of pelts for chrome tannage. The chrome tanner who fellmongered his own skins would pickle his pelts even if he did not intend to store them at all. The pickling given in this case is, however, much lighter than is given for storage, and is therefore of very little interest to the New Zealand fellmonger. But it is interesting to note that pickling serves, in some cases, a purpose other than the preservation of the pelts during storage.

The normal pickling procedure in the fellmongery is to add the salt to the dolly, then put in the pelts, and finally add the acid. With this procedure, the pelts do not acid-swell at all, since the salt represses the swelling right from the beginning.

Let us now consider what happens to the salt in the pickle liquor. The pelts, when they come into the dolly, contain fairly large amounts of water. During pickling, the water diffuses out of the pelts into the liquor while the liquor diffuses into the pelts. This process goes on until the concentration of salt in the liquor inside the pelts is the same as it is in the dolly liquor outside. When this condition has been reached, pickling is complete as far as the salt is concerned. You can follow the process with a hydrometer if you like, but you must make sure that all the salt in the dolly is dissolved before you put the pelts in. Note the density of the pickle liquor as shown on the hydrometer. Put the pelts in and continue taking hydrometer readings at intervals. The density will fall rapidly at first as the liquor is diluted by the water from the pelts. As time goes on it will fall more and more slowly until, after about an hour, it will remain steady. This means, of course, that the salt concentration is the same inside and outside the pelts or, as the chemist puts it, "equilibrium has been reached". Salt does not combine with the pelt substance, and is present in the pickled pelt simply dissolved in the liquor it contains.

With the acid, however, the story is a little different. The delimed pelt is still slightly alkaline and still contains a certain amount of combined lime. When the acid from the pickle liquor diffuses into the pelt, it first of all combines with the lime and removes it as calcium sulphate. If the pelts have been properly delimed, they will contain only very small amounts of lime, and the small quantity of calcium sulphate formed can dissolve in and become distributed through the pickle liquor. The amount of calcium sulphate remaining in the pelts is negligible. But if deliming has been incomplete, large amounts of calcium sulphate will be formed. These will deposit as a heavy sludge and will build up an incrustation on the inside of the dolly and on the paddles. It is even more important to note that excessive calcium sulphate can deposit in the pelt itself, giving it a harsh, rough texture. It is not good practice to delime in the pickle dolly.

As the acid neutralises the lime, it takes the place of the lime and combines chemically with the collagen of the pelt. The first lots of acid diffusing into the pelt are therefore neutralised either by the lime or the collagen, and do nothing towards raising the acidity of the liquor held by the pelt. During the early stages of pickling, acid is being removed from the pickle liquor, but is not appearing in the pelt liquor. Pelts can, in fact, absorb about 0·6 per cent of their weight of acid without leaving any free acid in the pelt liquor. As soon as the lime is completely neutralised and the acid requirements of the pelt proteins are satisfied, however, this process stops. From then on, the acidity of the liquor inside the pelt builds up until it is the same as that of the pickle liquor outside. The latter part of the process is thus the same as it is with the salt. In the same way, too, the absorption of acid from the pickle liquor is rapid at first, but slower and slower as pickling nears completion. The absorption of acid is rather faster than that of salt, and is complete in a slightly shorter time.

Paddling is usually continued for about two hours to ensure that the pickling is completely finished. By this time, equilibrium will have been reached for both the acid and the salt, and the liquor inside the pelt will have the same composition as the liquor in the dolly. The pelts can then be taken out, drained, and packed.

Now, it is the composition of the liquor held in the pelts which determines whether they will keep well during storage or whether they will deteriorate. It is this liquor which permeates the whole of the pickled pelt and which can either preserve the collagen fibres it surrounds or bring about their destruction. Temperature is the only other factor which can affect the pelts. The composition of the pelt liquor is therefore of prime importance to the fellmonger, and must be controlled by him very carefully indeed. It is fortunate that, when pickling is complete, the liquor in the dolly has the same composition as the pelt liquor. This means that the fellmonger can get the information he requires about the pelt liquor by testing the pickle liquor left in the dolly. He can find out its salt content by means of a hydrometer and its acid content by titration with standard caustic soda. If he had to obtain this information by testing the pelt instead of the pickle liquor, he would have a much more difficult task, and he would almost certainly need to have his tests done in a laboratory. As it is, he can determine the acid and salt in the pelt liquor relatively easily, the main condition being that the tests must be made only when the dolly has been running long enough for the liquor to be the same inside and outside the pelts. If the dolly has been running for more than half an hour, the results will be very close to the final figures, since, as we mentioned earlier, the changes towards the end of pickling are very slight. The results will certainly be accurate enough to show whether more acid or salt is required, and the composition of the liquor can therefore be corrected in time to finish pickling in the normal two hours. It must be emphasised again that it is the composition of the pelt liquor which is important, and not the composition of the pickle liquor as such. It is thus useless testing the pickle liquor unless it has the same composition as the pelt liquor. This is ensured by allowing sufficient time for the two to come to equilibrium.

So far we have not discussed what concentrations of salt and acid we should have in the liquor of the pickled pelt if we want to maintain its quality during storage. Let us first of all look at the dangers of using too little and too much of each constituent separately and of both together. These can be set out in a table, as follows:

PICKLE	FAULT IN PELTS
Excess of acid	Acid damage to pelt collagen
Excess of acid and excess of salt	Excessive acid damage
Excess of salt	Pelt of poor microstructure
Deficiency of acid and excess of salt	Pelt of poor microstructure
Deficiency of acid	Mould growth
Deficiency of acid and deficiency of salt	Putrefaction and mould growth
Deficiency of salt	Mould growth and acid damage
Excess of acid and deficiency of salt	Excessive acid damage

The "acid damage" referred to above is actual destruction of the pelt collagen, which, as we have already seen, takes place when the acid is too concentrated. Excessive salt leads to splitting of the collagen fibres and to lack of cohesion in the structure of the pelt. This is described as "poor microstructure" in the table.

It will thus be seen that trouble can occur with too much or too little of both acid and salt. Up till a few years ago, it was generally accepted both here and overseas that if the spent pickle liquor contained 9–10 per cent of salt and 0·8–1 per cent of sulphuric acid, the pelts could be stored for at least a year without any apparent deterioration. Of course, tanners overseas could not readily test the pelt liquor of the pelts they bought, because it is difficult, if not impossible, to squeeze sufficient liquor from the pelts after they have been casked for any length of time. The overseas tanners had to test the acid and salt contents of the pelts themselves and then try to calculate what the composition of the pelt liquor was. This is not a satisfactory procedure for reasons which we need not discuss here. Testing the spent liquor or the liquor squeezed out from the pelts gives a much more reliable result.

You will have noticed that the overseas recommendation of 9–10 per cent of salt is rather lower than the 12–14 per cent generally found in New Zealand pickle liquors, but the slightly higher concentration used here is not enough to do any harm. As far as the acid is concerned, it is interesting, in view of what is to come later, that an acid concentration as low as 0·4 per cent was quite common in New Zealand at one time. Complaints of mould growth and pressure from overseas tanners forced fellmongers here to raise the acid concentration in an attempt to overcome the trouble. The attempt was never wholly successful and, even at 1 per cent acidity, occasional complaints about mould growth have been experienced. This is not altogether surprising since moulds such as *Alternaria tenuis,* which we mentioned earlier, can stand more than 1 per cent of acid. Recent work in New Zealand has shown, however, that the figure of 0·8–1 per cent for acid is too high and that, under the conditions of storage and transport of New Zealand pelts, acid damage can and does occur when this concentration of acid is used. But we shall leave the discussion of these investigations until we have dealt with the conditions of storage and transport in general.

One of the main dangers to pickled pelts while they are still in the fellmongery is water. If the pelts are splashed with water, the pelt liquor is diluted down wherever the water touches them, and the effect is the same as if those spots had been underpickled. The water splashes are liable to show up later as patches of mould or of bacterial decomposition. The hosing of floors or machinery in the vicinity of pickled pelts should be strictly forbidden.

The casks themselves are also a source of danger. Being made of wood which is a porous substance, the casks are capable of absorbing quite large quantities of pelt liquor. When they do this, they leave the outside layer of pelts short of liquor and therefore liable to mould growth. This trouble can be avoided either by soaking the casks with pickle liquor prior to filling, or by packing the cask with wet pelts which have not been stacked in bins to drain. In the latter case, the excess liquor runs out of the pelts and saturates the cask.

Storing the casked pelts outside, as is common practice in New Zealand fellmongeries and in overseas tanneries, exposes them to still further dangers. In the first place, pelt liquor soaks through the casks and is evaporated from the surface. You will all have seen salt on the outsides of casks which have been lying in the open for any length of time. Then, too, alternate wetting and drying can open up the staves, allowing rain to leak through into the pelts or else permitting the pelts to dry out. Admittedly, if the casks are sound, the damage caused by the weather is usually not great, but the danger is always there, and the casks are certainly not improved by the treatment. Covered storage should certainly be provided for casked pelts.

But the effects of the weather on the pelts, undesirable as they may be, are by no means the worst. Temperature effects are very much more severe and widespread. Although the deleterious effect of heat on pickled pelts has been recognised for a very long time and is mentioned in all the textbooks, the statement has always been made that if the pelts were pickled in a liquor of the recommended composition, they would not be affected by ordinary conditions of storage temperature. Recent work in New Zealand has shown, however, that deterioration can take place at temperatures normally encountered during storage in this country and during transport to overseas markets, even although the pickling has been carried out as recommended by overseas authorities. This work has also shown that the effect of temperature on the pelts is intimately bound up with the acidity of the pelt liquor.

The story of the New Zealand investigation starts with the shipping strike in 1951, following which the normal transport arrangements were upset, and in consequence of which some pelts were shipped overseas in unsuitable stowage. Complaints from the buyers were numerous and serious. In the worst cases, the casks contained what could only be described as a brown mush with scarcely any sign of pelt structure at all. The buyers tended to blame the New Zealand fellmongers for the trouble, so tests were made here in an attempt to discover the cause. It was soon found that heat would produce all the effects complained of, and that the temperatures necessary were surprisingly low. It was also found that the acidity of the pelt liquor played a not inconsiderable part. The higher the acidity, the more sensitive the pelts were to heat. The outbreak of pelt damage following the shipping strike was undoubtedly due to high temperatures aboard ship. But since such gross damage could be caused by only moderately high temperatures, it seemed likely that lesser damage, not visible on inspection, but nevertheless affecting the quality of the pelts, might occur at considerably lower temperatures. It was therefore decided to make a full investigation into the effect of acid and heat on pickled pelts.

The problem was to find a method of detecting this damage in its early stages, before it was easily recognisable. Fortunately, such a method had recently been worked out by some English chemists. To understand it, we must once again consider the nature of the pickled pelt. The protein of a freshly pickled pelt consists almost entirely of collagen which is, of course, insoluble in water. If we neutralise the acid in a piece of pelt and then extract it with water, collagen itself will not dissolve, but any decomposed protein matter will. We may as well use the tanner's term "hide substance" for the protein matter of the pelt when we are referring to the pelt proteins in general and not to any one protein in particular. The amount of hide substance which will dissolve in water, then, gives a measure of the acid damage which has taken place and, to enable comparisons to be made, the soluble hide substance is expressed as a percentage of the total hide substance in the pelt. This ratio of soluble hide substance to total hide substance makes it possible to detect and measure decomposition of the pelt collagen or damage to the pelt structure long before there is any visible effect. In various publications, you may find the ratio expressed in various ways:

Soluble hide substance/total hide substance,
Soluble nitrogen/total nitrogen, or
Soluble protein/total protein.

All these expressions mean exactly the same thing – the percentage of the protein matter which has been attacked and made soluble in water.

It should be explained, too, that although freshly pickled pelt contains very little decomposed collagen, it does contain 1–3 per cent of its hide substance in the soluble form, probably because the interfibrillary matter has not been completely removed during deliming. If more than about 3 per cent of the total hide substance of a pelt is soluble, however, we can be reasonably sure that acid damage to the collagen has taken place. When the soluble hide substance forms 8 per cent of the total hide substance, the pelt will be tender and would probably give rise to complaints from the buyer. At 20 per cent soluble hide substance, disintegration of the pelt structure will be clearly discernible, and at 40 per cent the pelt will have fallen to pieces and will be scarcely recognisable as pelt at all.

Using the percentage of soluble hide substance, then, as a measure of pelt damage, a very comprehensive investigation was made into the effect of temperature on pelts at various acidities. A number of freezing works supplied the pelts which were thus representative of production from all parts of the country. The results were surprising and somewhat disconcerting.

It was found that pelts stored at 37°F would keep in good condition for long periods, even when the acid content of the spent pickle liquor was 1 per cent. If it were practical or economical to handle and transport pelts as refrigerated cargo, neither moulds nor acid damage would be a problem.

At 68°F damage to the pelts occurred at a slow but steady rate. With 1 per cent of acid in the spent pickle liquor, the percentage of soluble hide substance rose by 5 per cent in 16 weeks. At this point, damage was just starting to become evident. The pelts were somewhat tender and easily torn. The important finding was, however, that the amount of damage was almost exactly proportional to the acidity of the spent pickle liquor. At 0·5 per cent acidity, the damage was only half as great (2·5 per cent extra soluble hide substance) and at 0·1 per cent acidity, it was only one-tenth as great (0·5 per cent extra soluble hide substance). Looked at another way, it would take 32 weeks at 0·5 per cent acid or 160 weeks at 0·1 per cent acid to get the same amount of damage as was produced in 16 weeks at 1 per cent acid.

When the pelts were stored at 100°F deterioration was much more rapid. At 1 per cent acid in the spent pickle liquor, the soluble hide substance rose 15 per cent in eight weeks. The deterioration was six times as rapid as at 68°F. The damage produced in 16 weeks at 68°F would be produced in less than three weeks at 100°F. Again, the damage was proportional to the acidity of the pickle liquor. At 0·1 per cent acid the soluble hide substance rose by only 1·5 per cent in the eight weeks. The pelts with 15 per cent extra soluble hide substance were, of course, badly discoloured and showed signs of deterioration.

The results quoted above are shown in fig. 6, which is a graph showing the damage done at various acidities in eight weeks at the three temperatures quoted.

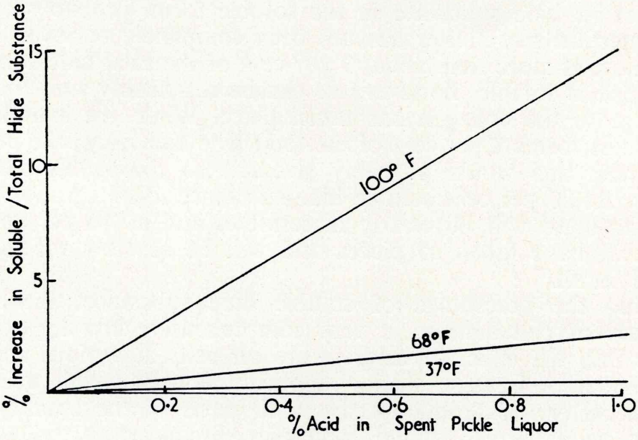


FIG. 6.

It might be as well at this point to emphasise that when we speak of "acidity" with regard to pelts, we mean the percentage of acid in the spent pickle liquor which, as we have seen, is the same as that in the liquor held by the pelts themselves. In America, it is apparently the practice to add the acid to the dolly before the pelts are put in, and Americans frequently quote the acidity as the percentage of acid in the pickle liquor before the pelts are added. The pelts will, of course, reduce the acidity very considerably, the exact reduction depending on the amount of pickle liquor, the weight of pelts put in, and the degree of deliming they have had before entering the pickle dolly. It is difficult to estimate just what the acidity of the spent pickle liquor would be, but it would certainly be much less than it was initially. If you are discussing acidities with anyone who quotes American figures, make sure that you are both talking about the same thing. You cannot compare figures for spent pickle liquor with those for an unused dolly. Another figure sometimes quoted is the percentage of acid in the pelt itself. Again, this depends on a number of factors, and cannot be compared directly with the spent pickle figure. It is easy to get at cross purposes with someone if you are not careful to define your terms.

The effect of the salt in the pickle liquor was also checked over the range 8–14 per cent. Inside this range, the percentage of salt made no measurable difference to the rate of deterioration of the pelt. The percentages of salt tested were all inside the limits recommended as safe by overseas chemists, and higher or lower percentages would probably have shown some effect. But the range tested covers all percentages likely to be encountered in practice in New Zealand. It therefore seemed unlikely that the present usage as regards salt was contributing to the damage.

The surprising thing is that pelts which had been considered correctly pickled by overseas and New Zealand standards should show measurable deterioration when stored for a relatively short period at a temperature as low as 68°F. Temperatures as high as this are quite common during the summer in New Zealand, and much higher temperatures are experienced during the passage of the pelts through the tropics on their way overseas. Pelts stored outside at Masterton showed average temperatures at the centre of the cask of 61°F during December, 65°F during January, and 69°F during February. The highest temperature reached at the centre of the cask was 76°F; near the top of the cask, it was 99°F. In view of the results obtained in the experiments at 68°F, these temperatures are far too high for safety. They reinforce strongly the argument in favour of covered storage for all casked pelts. As regards transport across the tropics, ships spend approximately seven days in waters where both sea and air temperatures are in the region of 80°F.

In view of all this, it is surprising that the dangers of a pickle liquor acidity of 1 per cent or thereabouts were not realised before. There are several reasons for this. In the first place, most of the investigations were carried out in England where temperatures are generally lower and where the interval between fellmongering and tanning is relatively short. Secondly, the use of the percentage of soluble hide substance to measure pelt damage is fairly recent. Previously, the pelts were judged on their physical properties or on their microstructure, neither of which is capable of detecting small amounts of damage. In many cases, pelts must have been classed as undamaged when, in fact, they had deteriorated to some extent at least. If the leather produced from the pelts was not quite as good as it should have been, this was simply put down to the poor type of pelts produced in New Zealand. It should be remembered, too, that pelts are normally exposed to elevated temperatures for only short periods and that, prior to the shipping strike, pelts were handled by experienced shippers who gave them reasonably cool stowage. Nevertheless, English tanners have for many years considered New Zealand pelts to be inferior in strength to their own production. This was simply considered to be a general property of New Zealand pelts, and no one thought to look for a cause. Then again, practically all freezing works have at one time or another received complaints about tender pelts. Various reasons have been put forward to explain this defect, but it now appears likely that most of the trouble has been due to the effect of temperature on high-acid pelts. It would seem as if almost all New Zealand pelts have suffered some damage before they have reached overseas markets, and that this is one of the reasons for the lower regard in which they have been held by English tanners. Occasionally, circumstances have been such that the damage was much more severe. Then the tanners complained. It took drastic conditions such as those following the shipping strike to bring the trouble forcibly to our notice.

There are two methods of improving the situation. In the first place, we can do something as regards temperature of storage. Casked pelts should be kept under cover, and as cool as possible. The shipping companies must be impressed with the importance of cool stowage for pelts. But this is not enough by itself. We must keep the acidity of the pickle liquor to as low a figure as possible. Every reduction in acidity means an increase in the safety margin for the pelts.

You will remember that the acid was raised originally in an endeavour to control mould growth. Although it was not 100 per cent successful, a high concentration of acid did have a retarding effect on mould growth. If we lower the acid, we must take steps to prevent a recurrence of this trouble. The obvious answer is to add to the pickle liquor some substance which will kill moulds. Such substances are called *fungicides*. Unfortunately, some of the most effective fungicides are insoluble in pickle liquor, and others have undesirable properties which affect the finished leather. Beta-Naphthol in a concentration of 0·05 per cent in the pickle liquor has been used quite satisfactorily for a number of years, but it has the slight disadvantage of forming an intense dark-blue colour with an impurity (nitrite) sometimes found in sulphuric acid. Paranitrophenol is another fungicide which is quite effective but, with certain types of tannage, it stains the leather yellow. 2.4.6. Trichlorphenol, commonly known as T.C.P., is effective at a concentration of 0·025 per cent and is free from these defects.

It would appear that the secret of successful pickling is to use the customary amount of salt, but to keep the acid as low as is practical, and to control mould growth by means of a fungicide. At all times and at all costs, pickled pelts must be kept cool. If these precautions are taken, we should be able to put into the hands of overseas tanners a product as good as the day it came out of the pickle dolly.

Chapter 6

PIEING

The traditional method of recovering the wool from lugs, codlocks, and other trimmings from the skins was by a bacterial loosening of the wool, and was a necessary, though not particularly pleasant, part of the fellmonger's work. It was carried out extensively in New Zealand and Australia, but was less common in England where, with the smaller scale of operations, the skins were trimmed less heavily and practically the whole of the wool could be recovered by painting and pulling. Bacterial pieing has practically died out in New Zealand in favour of the mechanical process described in the last section of this chapter. It is still extensively practised in Australia, although some Slipemaster machines have been installed.

Pieing is essentially a bacterial process. It consists of supplying warmth and moisture and of making conditions generally suitable for the growth of those bacteria which attack and digest skin, but leave the wool relatively undamaged. The bacteria, by the way, are able to digest the skin because they secrete proteolytic enzymes. We may therefore look on pieing as being an enzyme digestion of the skin, the enzymes being produced on the spot by the bacteria which are encouraged to grow there.

Originally, the decomposition of the skin was allowed to proceed only far enough to loosen the wool which was then "picked" from the pieces. The process was thus almost exactly the same as the "sweating" of whole skins. Until recently this procedure was still used in New Zealand for the lugs and for pieces carrying the better grades of wool. Owing to the very unpleasant nature of pie picking, difficulty was experienced in getting labour, and the practice grew up of letting the digestion of the skin go through to completion. The wool could then be washed free of decomposed and disintegrated skin. This method was known as "pieing right out" and became the usual New Zealand method of dealing with skin pieces carrying lower grades of wool. Owing to the more severe digestion process, the wool tended to be more discoloured and of a lower quality than that recovered by picking.

Up till the time when pieing was replaced by the Slipemaster, there were two main methods of pieing in use in New Zealand. Only a brief outline of the processes will be given here, because they are now of only historical interest. They were:

Floor Pieing

The wet skin pieces were spread on the floor and allowed to lie there until digestion of the skin had reached the desired stage. The pieces heated up, and the temperature was controlled by adjusting the depth of the layer, by turning the pieces over and by spraying with cold water when necessary. This required frequent attention and considerable experience on the part of the operator. The pieces could be picked or pied right out. In the latter case, the temperature was allowed to rise rather higher and the digestion was allowed to proceed for a longer time. Apart from the unsavoury nature of the work, the main disadvantages were the large floor space required and the difficulty of controlling the temperature.

Tank Pieing

This was a later development. The pieces were digested under water in concrete tanks about 3 ft deep, the water being changed as necessary. Warm water was used, and the temperature was adjusted according to the speed and degree of digestion required. Pieces could be picked or pied right out, higher temperatures being used in the latter case. With this method less floor space was required, temperatures were more easily controlled, and the process was slightly, though only slightly, less unpleasant.

Wool recovered by both these methods, and especially by tank pieing, was liable to spontaneous combustion due to the presence of body fat in the wool. The membranes surrounding the body fat were digested away during pieing and the fat was free to spread through the wool. Pie wool therefore had to be scoured to a low fat content in order to minimise the fire hazard. Few freezing works have operated for any length of time in the past without at least one pie-wool fire, and many fires on board ship have had their origin in pie wool.

AUSTRALIAN PROCESSES

A considerable amount of work has been done on the pieing process in Australia and some notable advances have been made. The first development was a process using a mould enzyme for the digestion of the skin. This, of course, did away with the necessity for using bacteria, and the unpleasant odours could be somewhat reduced. It was found that the enzyme worked much better if the skin pieces were shrunk by treatment with hot water at about 170°F prior to digestion. The enzyme digestion itself was carried out at about 100°F. Owing to the high cost of the mould enzyme, however, the process has not been used commercially to any extent in Australia.

But it was also found that shrinking the skin pieces in hot water speeded up ordinary tank pieing as well. Most of the Australian pie wool is now produced by pretreating the skin pieces in water at 170°F, and then tank pieing in warm water at about 100°F. Recent improvements to the process include aerating the water in the tanks to encourage the growth of desirable bacteria and adding calcium chloride to the water if it is not naturally hard.

SLIPEMASTER

It was accidentally discovered in New Zealand in 1949 that the wool could be removed mechanically from skin pieces after they had been shrunk in hot water. The shrinking toughens the skin and curls it up into a roll with the wool outwards. The wool can then be plucked by means of a set of squeeze rollers, the wool passing through, and the denuded skin remaining on the feed side of the rollers. A machine, known as the "Slipemaster", has been designed to shrink and pluck the skin pieces in one continuous operation. Apart from its other advantages, this process produces a wool free from body fat and, so long as certain elementary precautions are observed, not liable to spontaneous combustion. The mechanical method does not involve any digestion or decomposition of the skin at all, and is not "pieing" in the strict sense of the word. The denuded skin is quite fresh and can be used for manure or glue manufacture. Freedom from unsavoury odours and from flies, although impossible to evaluate in terms of money, are nevertheless very real advantages of the system.

Chapter 7

THE INTERPRETATION OF PHOTOMICROGRAPHS

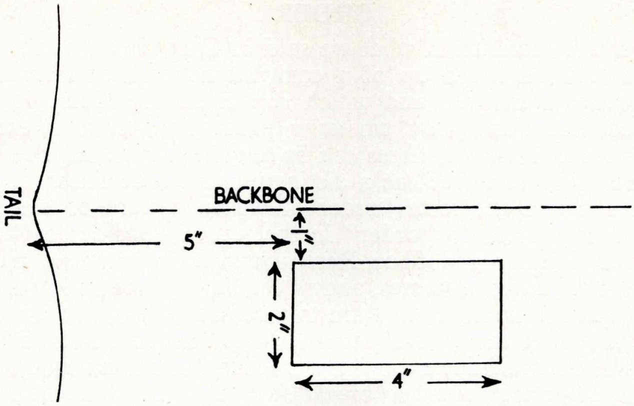
As we mentioned in Chapter 3, the examination of the fibre structure of a pelt under the microscope is of very great help to the fellmonger in judging whether the pelt has been correctly limed or not. Such an examination will show whether liming has been excessive or deficient, whether the pelt has been subjected to undue mechanical action, and whether it will make weak or strong leather.

The preparation of a pelt sample for microscopic examination is not an easy or simple procedure and it is unlikely that any fellmonger will attempt to do it himself. We shall not therefore bother with a detailed description of the procedure, but shall merely mention that it consists of toughening a piece of pelt for several days in formalin, freezing it, cutting it into thin slices with a special machine called a microtome, and then mounting the slices on microscope slides. New Zealand fellmongers are fortunate in that they can send samples of their pelts to the New Zealand Leather and Shoe Research Association which will do all this for them and will send them a report on the microstructure of the pelts, accompanied by photomicrographs.

Since the fibre structure varies from place to place in a pelt, it is essential that the samples sent for examination be taken always from the same position, otherwise comparisons of one pelt with another are impossible to make. It has been found that the most useful information can be obtained from a sample taken from a position *1 in. from the backbone* and *5 in. from the base of the tail*. The sample should be 4 in. long parallel to the backbone and 2 in. wide.

Again, since there is considerable natural variation from pelt to pelt, it is impossible to judge the quality of the processing by examining a sample from only one pelt. It is therefore necessary to send six samples from different pelts, all the samples being taken from the correct position on the pelt.

Too many fellmongers, when they receive reports on the microstructure of their pelts, are content to accept the reports and to ignore the photomicrographs as being too difficult for them to understand. While it is true that the interpretation of pelt micro-



structure needs a good deal of experience and can be done much more reliably by the expert, nevertheless the fellmonger loses much of the value of the report if he does not examine the photographs and see for himself the features on which the assessment has been made. It is not as difficult as most fellmongers appear to think.

But, first of all, a word of caution. The photograph which accompanies the assessment of your pelt structure shows the pelt magnified 100 times and represents a piece of pelt about $^4/_{100}$ in. by $^3/_{100}$ in. and $^1/_{250}$ in. thick. The assessment is, however, not based on only this one minute portion of the pelt sample. The slice of pelt actually put on the microscope slide is about $\frac{1}{2}$ in. by $\frac{1}{8}$ in. so that there are about 50 views of the same size as that shown in the photograph in each slice of pelt examined under the microscope. Several such $\frac{1}{2}$ in. by $\frac{1}{8}$ in. slices are cut from each sample. By the time the assessor has examined a number of slices from each of the six samples submitted, he has covered a considerable area of pelt and can form a very accurate judgment on the quality of the processing. He selects for photographing one view of one of the slices of one of the samples which, in his opinion, best illustrates the features of the samples as a whole, but his assessment of the pelt structure is by no means based on this view only. You should bear this in mind when comparing the expert's assessment with what you can see in the photomicrograph.

The New Zealand Leather and Shoe Research Association assessment of pelt structure is given under four headings:

Order.
Plumpness.
Separation.
Splitting.

We shall now consider each of these in turn and illustrate them with photomicrographs of actual pelts.

ORDER

You will recall from what we said in Chapter 1 that the dermis or true skin is made up of a complex network of fibre bundles which are interwoven and which run in all directions. It will be realised, therefore, that whatever plane of a skin is examined under the microscope, fibres can be seen in that plane. The pattern formed by these fibres has a distinguishable orderliness, and from this we derive the term "order of weave pattern of the fibres". This is contracted to "order" in the reports sent out by the New Zealand Leather and Shoe Research Association. The object of the fellmongering processes, and of the liming process in particular, is to open up the fibre structure to a certain extent, but it is equally important that the weave pattern should be disturbed as little as possible. A breakdown of the fibre bundles means loss of order in the structure; such a breakdown may be due to excessive alkalinity or to excessive paddling or to both. Continuous paddling in the lime dolly always leads to poorly structured pelts.

As most of you know, the New Zealand Leather and Shoe Research Association classifies the order of the weave pattern by means of the letters "G", "F", and "P", which stand for "Good", "Fair", and "Poor" respectively. Intermediate classifications are given the symbols "F+" which is between "Good" and "Fair", and "F−" which is between "Fair" and "Poor". The whole range is thus: G, F+, F, F−, P.

Now look at plates 7, 8, and 9, which illustrate pelts having "Good", "Fair", and "Poor" order respectively. The differences between them are more clearly seen in plates 7A, 8A, and 9A, which show the outlines of the fibre structures in the photomicrographs. The decrease in orderliness from plate 7, where the fibre pattern is compact and orderly, to plate 9, where the fibre pattern is almost non-existent, is obvious to anyone.

PLUMPNESS

Plumpness is, of course, a measure of thickness, so the plumpness of fibre bundles is judged by the diameter of their cross-sections. But there are natural variations in the thickness of fibre bundles. For instance, those in a lambskin are thinner than those in the skin of a mature sheep, and since what we really want to assess is how much the fibres have been plumped during liming, we have to allow for these natural variations. Therefore, in assessing plumpness, the appearance of turgidity or distension of the fibres, together with the thickness of outline, are taken into account. Pelts are graded "G", "F", and "P" for plumpness in exactly the same way as for order. Plates 7, 8, and 9 also show these three degrees of plumpness.

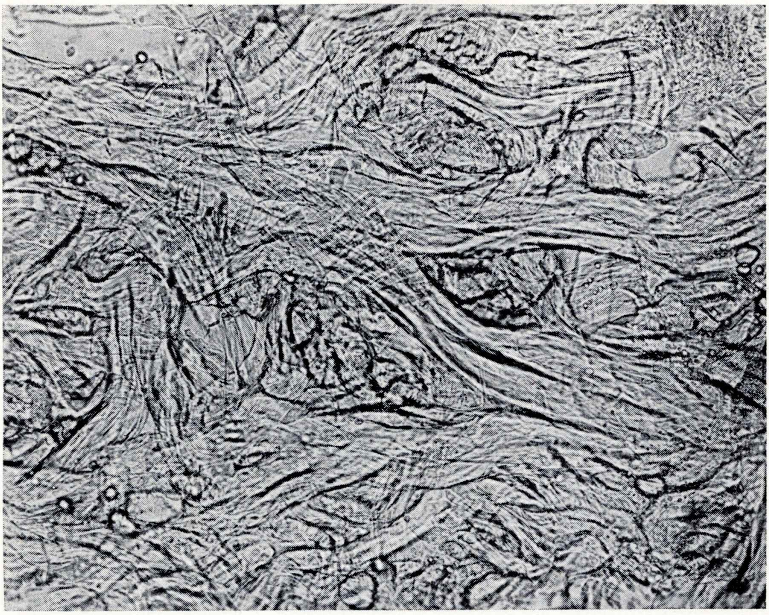


PLATE 7. Stout fibres; compacted and orderly fibre pattern; some separation and splitting of fibre bundles.

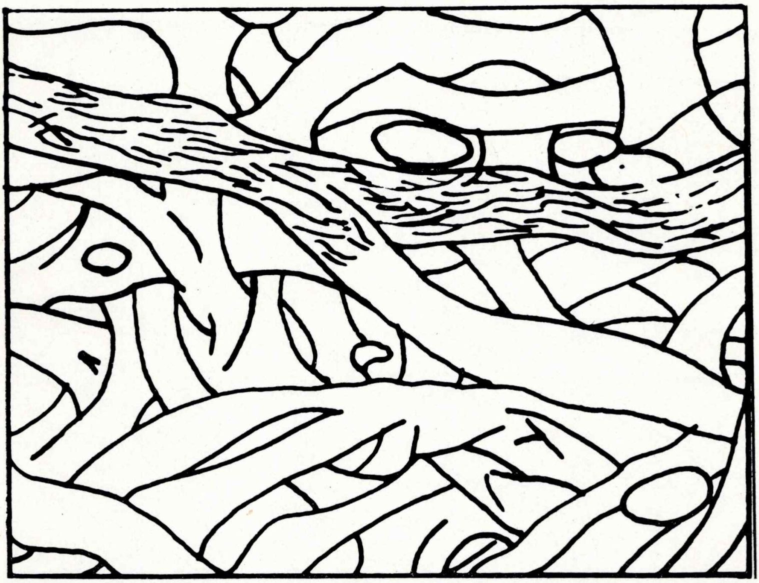


PLATE 7A. Outline of fibre pattern shown in plate 7; splitting of one fibre bundle also shown.

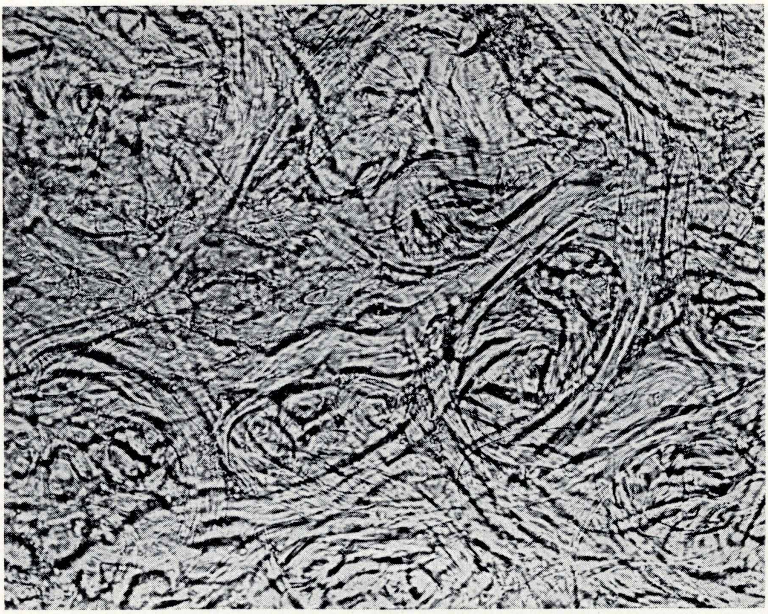


PLATE 8. Fibre pattern less orderly; more separation and splitting up of fibre bundles; fibre bundles not as stout as those shown in plate 7.

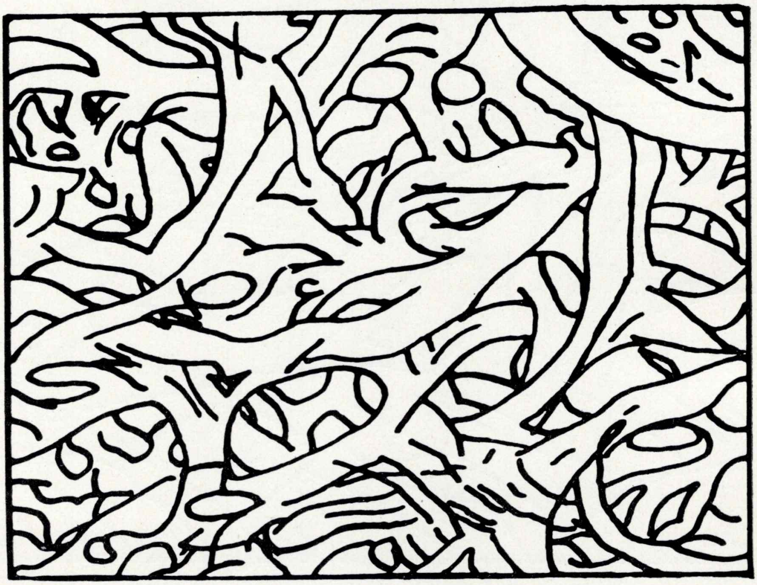


PLATE 8A. Outline of fibre pattern shown in plate 8

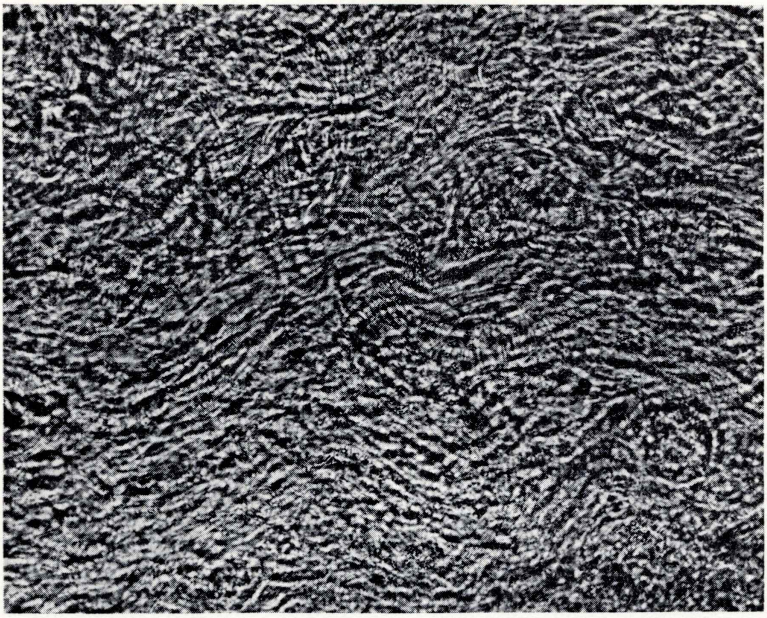


PLATE 9. Fibre pattern almost non-existent; excessive separation and splitting up of fibre bundles.

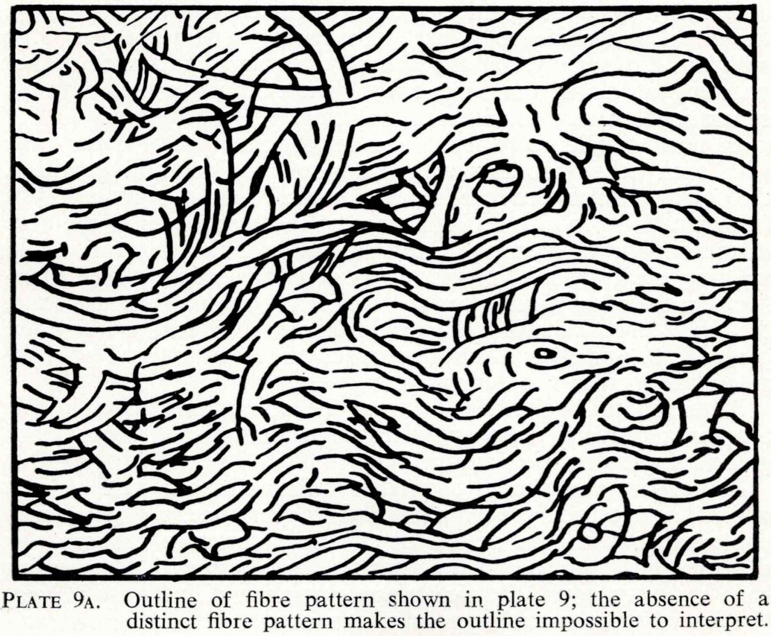


PLATE 9A. Outline of fibre pattern shown in plate 9; the absence of a distinct fibre pattern makes the outline impossible to interpret.

SEPARATION AND SPLITTING

We have already explained in Chapter 1 how separation and splitting differ from each other, and we need only remind you that separation is the parting of the fibres and fibre bundles one from another and that splitting is the freeing of the unit fibrils within the fibres. Separation is caused mainly by mechanical action in the limed condition, while splitting is caused by the chemical action of the alkali in the lime liquor. Splitting is seen in photomicrographs as a series of striations inside the fibres and parallel to their length.

The assessments for both separation and splitting are given in terms of "+" and "−" signs. Excessive amounts of either are shown as "++", and complete absence as "−". The complete range with intermediate classifications is: ++, +±, +, ±, =.

As has been mentioned already, a moderate degree of separation and splitting is desirable in a pelt, so that the tanning materials will be able to penetrate and combine with the fibre structure. An underlimed pelt with a classification of "−" for separation and splitting would therefore not tan properly. On the other hand, an overlimed pelt with a classification of "++" would have had its fibre structure so weakened that it would make a poor leather. A good assessment for separation and splitting is "+" or "±".

Although pelts normally show similar degrees of both separation and splitting, it is possible, by the use of a mild alkali such as sodium hydrosulphide and by excessive paddling in the lime dolly, to get a pelt showing a large amount of separation and little splitting. Conversely, by the use of a strong alkali and by not paddling at all in the lime dolly, you can get a pelt with no separation but very considerable splitting.

In normal pelts, separation and splitting run parallel not only with each other but also with orderliness. Alkali and paddling, the factors which produce separation and splitting, are also the factors which produce a disturbance of the orderliness of the fibre structure. For this reason, a pelt section in which separation and splitting are excessive always shows a poorly ordered fibre structure. On the other hand, when separation and splitting are moderate, the fibre structure will be orderly. Because of this, we can use plates 7, 8, and 9 to illustrate degrees of separation and splitting as well as degrees of order and plumpness.

Plates 10 to 14 further illustrate the points mentioned in this chapter and merit close and detailed examination. The captions give all the information required.

Photomicrographs can give other information as well. A pelt which has not been properly delimed, for instance, will give fuzzy photographs with the details of the fibre structure obscured by the interfibrillary matter which has not been removed. Pelts which have had very severe chemical abuse may show disintegrated fibres. Neither of these should appear in commercial pelts, however, and the main value of microscopic examination is to help the fellmonger to determine whether or not the liming process has been correctly and efficiently carried out.

If you care to study this chapter and especially the photomicrographs which go with it, you will be in a better position to derive the full value from the reports you receive on the microstructure of your pelts.

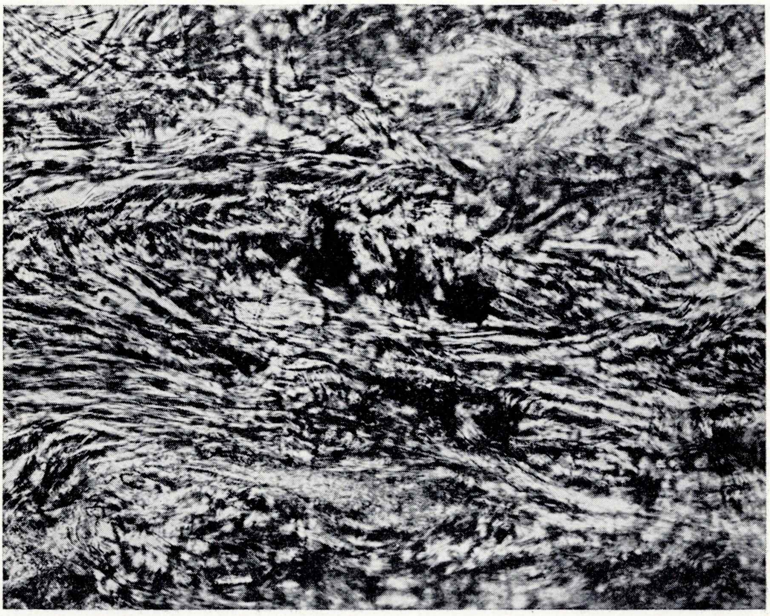


PLATE 10. Corium fibres of raw skin enlarged, showing weave pattern and unplumped, unopened fibres.

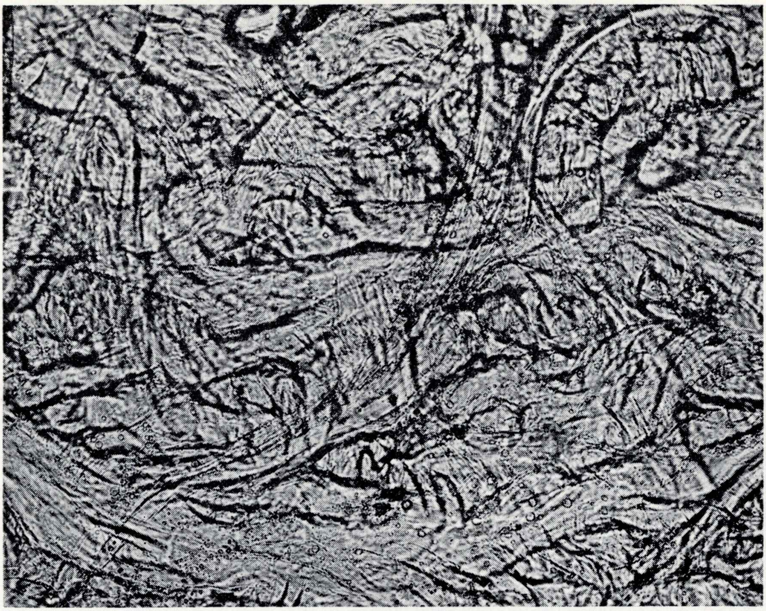


PLATE 11. Plump but unopened corium fibres in pickled pelt after weak liming.

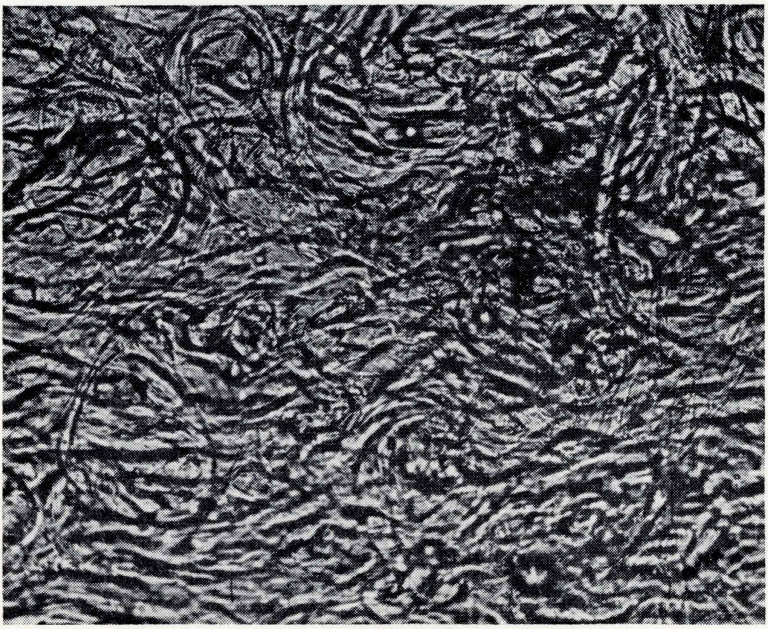


PLATE 12. Disordered weave in corium fibres of pickled pelt resulting from much agitation during a strong sulphide liming.

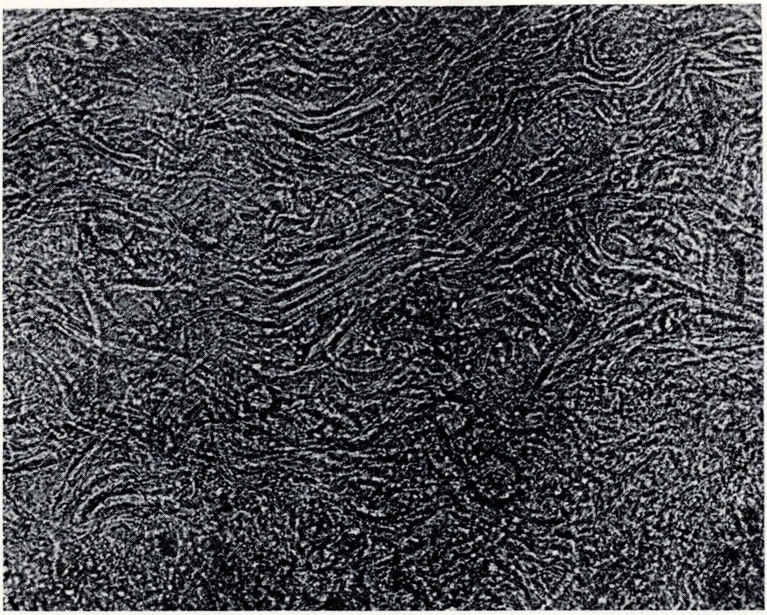


PLATE 13. Fine splitting of corium fibres into fibrils in a commercial pelt.

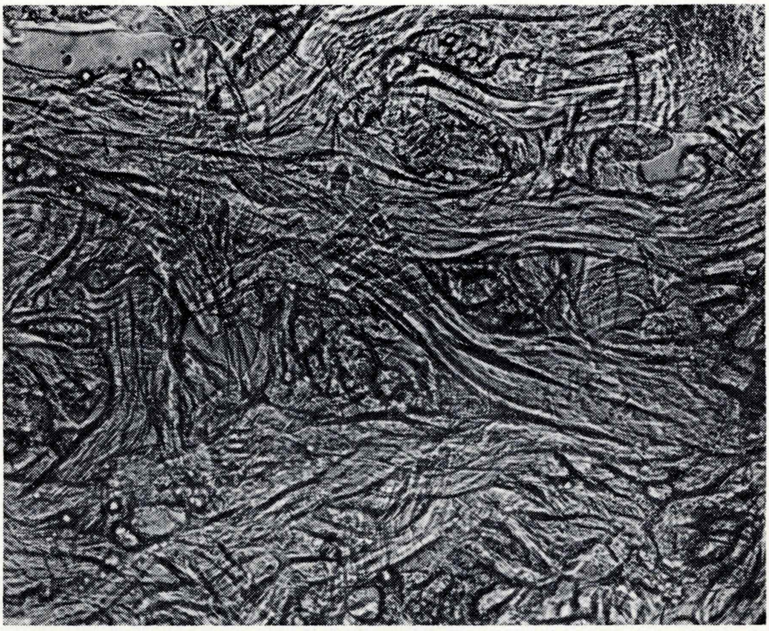


PLATE 14. Corium fibre structure 6 in. from the tail and 1 in. from the backbone, showing stout fibres and a compact, orderly weave.

Chapter 8

THE TANNING OF LIGHT LEATHERS

The fellmonger may be interested to learn something of the various leathers which are made from his pickled pelts and to be given a very brief outline of the methods by which they are prepared.

The bulk of the lamb pelts exported to the United States are made into grain or suede clothing leathers, but other leathers made from New Zealand sheep and lamb pelts include shoe linings and sockings, slipper uppers, gas-meter diaphragms, roller leathers, gloving leathers (grain and suede), chamois, doeskin, hat leathers, leathers for fancy goods, handbags, and wallets, bookbinding, and surgical appliances.

The main tanning methods used for light leathers are:

Vegetable.
Chrome.
Semi-chrome.
Oil.
Formaldehyde.

Before describing each of these tannages briefly, it will be as well to mention two preliminary treatments which are frequently given to pelts in the tannery before they are actually tanned.

Splitting. The heavier sheep pelts can be split to give a flesh and a grain which are used for different purposes. The pickled pelts are placed in water, which removes some of the salt and allows the pelt to swell. After stacking overnight, the swollen pelts are put through a splitting machine which consists essentially of two rollers feeding the pelt on to a moving band knife which cuts the skin into two layers. The flesh layer is usually converted into chamois, while the grain layer is vegetable tanned to produce a skiver.

Degreasing. For most purposes the pelts are degreased with kerosene prior to tanning. The pelts are allowed to dry out to 50 per cent moisture or less, and are then drummed with warm kerosene and a wetting agent. Most of the kerosene-water emulsion is then removed by wringing or by a warm, salt-water wash or by both. This degreasing process is not very efficient, and the value of the treatment is in equalising the distribution of grease in the skin rather than in achieving a complete removal. More efficient removal of the grease can be obtained by solvent extraction of the dry, tanned skins using white spirit.

VEGETABLE TANNING

Many trees and shrubs contain substances which can combine with collagen and give it the properties of leather. Those commonly used are sulphited quebracho, mimosa, and myrobalans.

The actual tanning is carried out in a drum or paddle, the tanning extract being added gradually until the desired degree of tanning has been achieved. The pelts are left in the liquor overnight, and are then drained and dried in a warm stove.

Vegetable tanning is used for shoe linings, roller leather, hat leather, fancy goods, and bookbinding, the last three being made from skivers obtained by splitting sheepskins. The vegetable tannage can be modified by a subsequent semi-chrome process to increase the resistance to perspiration where the leather is to be used in shoes. Full skins are also vegetable tanned to give basils or roans. For specialised products such as roller leathers, a very firm leather is required. This is produced by means of an oak-bark tannage or by heavy filling of the tighter textured vegetable-tanned basils. Gas-meter diaphragms, which are used to control the flow of gas, are made to a strict specification. They must be free from holes such as pinhole, and after vegetable tanning are semi-chrome tanned to increase their durability.

CHROME TANNING

For chrome tanning the pelts are degreased and then put into a drum to which chromium salts are added in stages. The leather usually stays in the drum overnight, after which it is removed from the drum and put aside to "age". During the ageing period, the chromium salts combine more firmly with the collagen. The leather is then shaved and put back into the drum to be neutralised with a weak alkali such as sodium bicarbonate or borax. After this, it is washed and "fat liquored" with special oils to give it flexibility. Washing and drying complete the process.

Leathers for clothing, gloving, and shoe linings can be chrome tanned to give the desired drape and plasticity. Shoe-lining leathers are chrome tanned to give a firm lining which will stand up to vulcanising temperatures.

SEMI-CHROME TANNING

In this process the leather is first vegetable tanned and then given a light chrome tanning. As we mentioned earlier, this gives increased resistance to perspiration in such products as shoe linings and hat leathers.

OIL TANNING

Oil tannage is used for the production of chamois leather from the flesh layers of split sheepskins or from lambskins which have had the grain layer removed in a special type of fleshing machine. Cod oil is used and is worked into the skins over a period of several days. The leather is then heated for some hours in a stove, "aged", soaked in warm water, pressed to remove some of the oil and water, soaked in warm water made alkaline with sodium bicarbonate, washed in warm water, drained, and dried.

Naturally, such a process is very expensive, and numerous short cuts have been devised. A common method is to combine the oil tannage with a formaldehyde tannage.

FORMALDEHYDE TANNING

Formaldehyde, or formalin, will tan pelts if the liquor is slightly alkaline. The tannage is carried out in a drum, and sodium bicarbonate is added to give an alkaline reaction. After standing all night in the liquor, the leather is removed from the drum and held for some days to "age". It is then washed and can be fat liquored for doeskins (white suede lambs) or oil tanned to give a combination chamois.

FAULTS

Faults in the finished leather which can be partly or wholly ascribed to faulty fellmongering are summarised below. Most of them have been dealt with in earlier chapters, but it is interesting to note that in many cases the same fault can also be produced in the tannery. It may not always be easy to distinguish between fellmongering and tanning damage in the finished leather.

Deteriorated Pelts. Pelts which have been stored for two years or more are usually considered difficult to split successfully. In most cases, this is probably due to deterioration caused by acid and heat in the manner which we have discussed in Chapter 5. Chamois leathers made from deteriorated pelts have weak-textured areas known as "windows" because they can be seen clearly when the leather is held up to the light and, of course, any leather made from pelts which have undergone acid deterioration will show weakness in some degree.

Drawn Grain. This can be caused by overheating in the bate dolly, but can also occur in the tannery due to overheating during degreasing, or to vegetable tan liquors which are too acid, or to the use of insufficient salts in the tanning bath.

Dull Grain. The term is self-explanatory, and the fault is usually due to excessive alkali in the painting and liming operations. Again, overheating of the alkali-swollen skins when warming up the bate liquor can cause this dull grain and the fault known as "leopard grain".

Lime Blast. This is a roughening of the grain due to the formation of microscopic crystals of calcium carbonate in the grain layer, but, as lime blast can be removed by pickling and depickling, it should not be a serious problem in New Zealand pelts.

Creases. The formation of creases is sometimes a cause of complaint. If the pickled pelts become dried out whilst in stack, creases can form which are difficult to remove. Likewise, skins stacked for splitting can become badly creased. Such creases can, however, be cleared by running the pelts or grains in water for a few minutes.

Natural Grease can cause difficulty, particularly when the skins are to be finished as suede. The buffing abrasive which is used to produce the suede finish burns the grease, leaving a dark, shiny area (wheel burn) which cannot be removed by subsequent processing. This can be caused by attempting to degrease the skins when they have not been held in the pickled condition for a sufficient period. It is necessary to hold pickled pelts for six weeks after processing to allow the fat cells to deteriorate and render their contents accessible to the kerosene or white spirit. Wheel burn can also be due to inefficient or insufficient degreasing in the tannery.

Salt Sprout. This shows as small broken areas on the grain and is caused by allowing pickled pelts to become too dry. Salt crystallises out and, as the crystals grow, they rupture the grain. In the fellmongery, pickled pelts should be protected from hot draughts whilst in the bins. At the tannery, great care is needed when reducing the moisture content of pickled pelts in the preliminary stages of degreasing.

Rough Suede. This fault is due to too deep penetration of the flesh side into the looser-woven area of the corium. It can be caused by setting fleshing machines too tight when fleshing big sheep and, of course, can also be caused by the mechanical work at the tannery. Bold, distorted necks which have been over-swollen in the liming stages make avoidance of this damage very difficult and restrict our outlets for sheep pelts.

Mould or Spotting. Patches or spots where certain varieties of mould have grown remain visible through to the finished leather. These can occur at all stages of processing unless adequate precautions are taken to keep a fungicide present. During the preliminary operations in the tannery, the fungicide which the fellmonger has used may be lost and, unless steps are taken to replace it, there will be a risk of moulds growing on wet chrome leather if it is allowed to stand about for any length of time. If the leather is already coloured, it is likely that the colour will be modified. Once this occurs, it is rarely possible to restore the colour.

Chapter 9

SLIPE WOOLS

Slipe wools represent a substantial contribution to New Zealand's export income. The annual production is in the neighbourhood of 70 million pounds weight, or about 16 per cent of the total wool production of the country.

We do not intend to give here a description of the classing of slipe wools or of the grades which are made, since these vary from one fellmongery to another throughout the country. In general, the grades are based on fineness of wool or "count", on length of staple, and on yield. A little information about the uses of slipe wools as contrasted with normal greasy wools may, however, be of interest.

Slipe wools differ from greasy wools in the following ways:

(a) Being mainly lamb wools, they are shorter in the staple than greasy wools and are therefore less suitable for combing and for use in the worsted trade. The great bulk of slipe wools is used in the "woollen" trade where shortness of staple is less of a disadvantage.

(b) All slipe wools contain lime to a greater or lesser extent, and this makes scouring somewhat more difficult. With the use of detergents instead of soap for scouring, however, this is not as troublesome as it used to be.

(c) Slipe wools tend to contain a certain amount of scud which can cause trouble in the carding machines at the woollen mills. In some mills the wool is passed through tightly set metal rollers which crush and powder the dried scud so that it is easily removed.

(d) Since the wool is no longer in the form of a fleece, it is impossible for the sorters in the woollen mills to class the wool into the very narrow grades which they use for the highest quality trade. This, as well as the short staple, limits the use of slipe wools. At the same time, it means that the fellmonger must maintain a high standard of classing, since it is difficult, if not impossible, to reclass slipe wool.

(e) Because slipe wool is washed on the skin, it gives a higher yield of clean, dry wool than does greasy wool.

(f) In some cases the wool may be contaminated with sodium sulphide from the paint which attacks it to some extent and makes it inclined to be tender.

In general slipe wools are used in the "woollen" (as contrasted with the "worsted") trade and are made into such materials as carpets, blankets, rugs, tweeds, socks, underwear, hosiery, etc. They are sometimes used by themselves, but are more often blended with other wools. By far the greatest proportion of New Zealand slipe wools go to the Yorkshire mills.

On the other hand, most of the pie wools are bought by the Continent. Just what uses they are put to appears to be somewhat of a mystery.

REGAIN OF WOOL

Most fellmongers will be familiar with the term "regain" and will know that it refers to the moisture content of wool, but a few words as to its significance may not be out of place.

Wool has the property of being able to absorb very large quantities of moisture without becoming wet to the touch. It is this property, of course, which makes wool such a valuable material for clothing, but it is the same property which makes it difficult to weigh wool on an equitable basis for sale. In contact with moist air, wool absorbs moisture and becomes heavier. In contact with dry air, it loses moisture and becomes lighter. 100 lb of wool weighed under moderate atmospheric conditions might easily weigh 105 lb in very damp conditions or 95 lb in very dry conditions. This effect is very marked when slipe wool is baled and weighed soon after coming from the drier where, as is all too common in New Zealand, it has been overdried. The bales will gain several pounds in weight during storage.

Obviously it would be possible to determine the weight of bone-dry wool in a bale and to sell on that basis. The actual weight of the bale at any particular time would then be of no significance. But wool is never used in a bone-dry condition, so that this weight would never correspond to an actual weight. What is therefore commonly done, especially with high-grade scoured wools, is to determine the weight of the wool when it is in equilibrium with air under normal conditions, and to sell it on the basis of that weight. In actual practice, air is considered to be "normal" when it has a temperature of 70°F and a relative humidity of 65 per cent. Under these conditions clean, scoured wool will have a moisture content corresponding to a regain of approximately 16 per cent. (We shall explain presently how this "regain" is calculated.) Owing to the presence of grease and other impurities, unscoured slipe wool has a regain under the standard conditions in the range of 11–14 per cent. But slipe wool is always sold on the basis of the actual weight of the bale, so that if the wool is overdry, the weight of the bale is less than it should be, and the financial return is also less than it should be. Obviously it is to the fellmonger's advantage to weigh his wool at the right moisture content, either by controlling his drier so that the wool is not overdried or, if this is not practicable, by storing the dried wool loosely in bins in a room where the humidity is not too low and where the wool can pick up moisture from the air.

Determination of Regain. The wool is sampled carefully and the sample is weighed. Let us call this weight the "original weight". The sample is then dried completely in a current of hot air and reweighed. This weight is the "bone-dry weight". The loss of weight is the "moisture". The "regain" is the weight of the "moisture" expressed as a percentage of the "bone-dry weight". In this, it differs from the normal "moisture content" which is the "moisture" expressed as a percentage of the "original weight".

Thus, if 100 lb of wool was found to contain 10 lb of moisture, the "moisture content" would be:

$$\frac{10}{100} \times \frac{100}{1} = \textit{10 per cent moisture content,}$$

but the "regain" would be:

$$\frac{10}{90} \times \frac{100}{1} = \textit{11·1 per cent regain.}$$

For 100 lb of wool containing 14 lb of moisture (bone-dry weight = 86 lb), the figures would be:

$$\frac{14}{100} \times \frac{100}{1} = \textit{14 per cent moisture content,}$$

and

$$\frac{14}{86} \times \frac{100}{1} = \textit{16·3 per cent regain.}$$

HEATING OF WOOL

Heating of wool in bins or in bales can take place due to two completely unconnected causes. We shall deal with each of these in turn.

Dampness. If wool is packed when it is damp it may heat up, mainly due to the action of bacteria. It is thus similar to the heating of a haystack. But there is no evidence that wool will actually catch fire with this type of heating, although it may heat sufficiently to decompose and be converted into a brown mush which is completely valueless. Heating caused by dampness can occur in any type of wool – greasy, slipe, or pie wool.

Spontaneous Combustion of Pie Wool. This type of heating is confined to pie wool, and is not found in greasy wool, slipe wool, or properly processed Slipemaster wool. It is due to the action of some, as yet undiscovered, constituents in the body fat which contaminates pie wool. The heating sometimes continues until the wool actually bursts into flame, and many fires in fellmongeries, wool stores, and ships have been traced to this cause. At present the only precaution possible against spontaneous combustion in pie wool is to scour it sufficiently to reduce the fat content of the wool to safe limits.

Appendix 1

CHEMICAL INFORMATION

Chemical Names and Formulae of Substances Encountered in Fellmongering

COMMON NAME	CHEMICAL NAME	FORMULA
Ammonia	Ammonia	NH_3
Sal ammoniac Muriate of ammonia	Ammonium chloride	NH_4Cl
Sulphate of ammonia	Ammonium sulphate	$(NH_4)_2SO_4$
Limestone Agricultural lime	Calcium carbonate	$CaCO_3$
Hydrated lime Slaked lime	Calcium hydroxide	$Ca(OH)_2$
Burnt lime Unslaked lime	Calcium oxide	CaO
Calcium chloride	Calcium chloride	$CaCl_2$
Calcium sulphate	Calcium sulphate	$CaSO_4$
Calcium hydrosulphide Calcium sulphydrate	Calcium hydrosulphide Calcium sulphydrate	$Ca(HS)_2$
Muriatic acid Spirits of salt	Hydrochloric acid	HCl
Caustic soda	Sodium hydroxide	$NaOH$
Common salt	Sodium chloride	$NaCl$
Sodium sulphide	Sodium sulphide	Na_2S
Sodium hydrosulphide Sodium sulphydrate	Sodium hydrosulphide Sodium sulphydrate	$NaHS$
Sulphuric acid Oil of vitriol	Sulphuric acid	H_2SO_4
Water	Water	H_2O

Equations for Reactions Occurring in Fellmongery Processes

Painting and Liming

$$Na_2S + H_2O = NaOH + NaHS$$
$$2NaHS + Ca(OH)_2 = Ca(HS)_2 + 2NaOH$$
$$2NaOH + CaCl_2 = Ca(OH)_2 + 2NaCl$$

Deliming

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O$$
$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O$$
$$Ca(OH)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_3 + 2H_2O$$

Molecular Weights

By means of the molecular weights of substances it is possible to calculate from an equation the weights of these substances which will react with each other. A table of the molecular weights of the substances used in fellmongering is given below and some examples are given to illustrate their use

FORMULA	MOL. WT.	FORMULA	MOL. WT.
NH_3	17	$Ca(HS)_2$	106
NH_4Cl	53·5	HCl	36·5
$(NH_4)_2SO_4$	132	$NaOH$	40
$CaCO_3$	100	$NaCl$	58·5
$Ca(OH)_2$	74	Na_2S	78
CaO	56	$NaHS$	56
$CaCl_2$	111	H_2SO_4	98
$CaSO_4$	136	H_2O	18

Examples

(1) $NaOH + HCl = NaCl + H_2O$
$40 + 36{\cdot}5 = 58{\cdot}5 + 18$
(2) $Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O$
$74 + 107 = 111 + 34 + 36$
(3) $Ca(OH)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_3 + 2H_2O$
$74 + 132 = 136 + 34 + 36$

You will notice that the weights on one side of the equation equal those on the other side, and it is essential that they do so. We cannot make or destroy matter by ordinary chemical reactions.

So long as you keep to the same weight units throughout, you can use any ones you like. In the above examples, you could use pounds or ounces or grammes according to the quantities you were dealing with.

Appendix 2

FELLMONGERY TESTS

The fellmonger carries out regularly two determinations during the course of his processing. The method of doing these is described below. Although the composition of the reagents is given, the fellmonger will normally have these made up for him by a laboratory.

SULPHIDE IN LIME LIQUORS

Reagents

Ammonia Buffer. Solution 0·5N with respect to ammonia and 0·25M with respect to ammonium chloride.

Standard Zinc Sulphate. 0·05M zinc sulphate (14·35 g of $ZnSO_4.7H_2O$ per litre).

Test Papers. Strips of filter paper or blotting paper soaked in 10 per cent lead acetate solution and dried.

Sampling

The dolly should be paddled for 10 minutes after washing out is completed or after any addition of sodium sulphide, so that the liquor is of uniform composition throughout. A sample of about 100 ml is taken and stood aside for a few minutes to allow the lime and other solids to settle. The clear top liquor is used for the titration.

Titration

Measure out exactly 25 ml of the clear liquor into a 250 ml conical flask and add 25 ml of the ammonia buffer. The well mixed solutions are then titrated with the standard zinc sulphate until no more soluble sulphide remains. The end point is ascertained by spotting with a glass rod on to a test paper until no *immediate* brown stain is produced.

Calculation

Each ml of zinc sulphate used represents 0·016 per cent of sodium sulphide in the lime liquor. The following table gives the percentage corresponding to the titration at intervals of 5 ml. Intermediate values can be readily calculated.

ML OF ZINC SULPHATE	PERCENTAGE OF SODIUM SULPHIDE
1	0·016
5	0·08
10	0·16
15	0·24
20	0·32
25	0·40

ACID IN PICKLE LIQUORS

Reagents

Standard Caustic Soda. 0.204N NaOH (N/4·9 NaOH).

Indicator. 1 per cent solution of phenolphthalein in alcohol or any other suitable indicator solution.

Titration

Measure out exactly 10 ml of pickle liquor, add a few drops of indicator, and titrate with standard caustic soda until the indicator changes colour. In the case of phenolphthalein the change is from colourless to pink.

Calculation

Each ml of caustic soda used represents 0·1 per cent of sulphuric acid in the pickle liquor. A titration of 10 ml = 1·0 per cent acid.

Notes

(1) The term "ml" used above is a contraction for "millilitres", which are virtually the same as cubic centimetres or "c.c.".

(2) The concentrations of the standard reagents and the volumes of the liquors can be varied if so desired, but the calculations may be slightly different from those given above. For instance, in testing pickle liquor, you could use 1·02N caustic soda and take 25 ml of pickle liquor for the test. In this case, each ml of caustic soda would represent 0·2 per cent of sulphuric acid, and a titration of 5 ml would equal 1·0 per cent of acid.

Appendix 3

SOME USEFUL TABLES

TEMPERATURE CONVERSION

In scientific publications the temperatures are usually given in degrees Centigrade, and the following table gives the conversion from Centigrade to the more familiar Fahrenheit. The general rule for conversion is to multiply Centigrade by 9, then divide by 5, and add 32 to the answer. For instance, to convert 120° Centigrade to Fahrenheit:

$$120 \times 9 = 1{,}080$$
$$1{,}080 \div 5 = 216$$
$$216 + 32 = 248$$
$$120^\circ\text{C} = 248^\circ\text{F}$$

°C	°F	°C	°F
−5	23	50	122
0	32	55	131
5	41	60	140
10	50	65	149
15	59	70	158
20	68	75	167
25	77	80	176
30	86	85	185
35	95	90	194
40	104	95	203
45	113	100	212

DENSITY CONVERSION

Some fellmongers use the Twaddel scale for making up their sodium sulphide solutions, while others use the Beaume scale. It is useful, when making comparisons, to know how one corresponds to the other. The following table gives the relationship between Twaddel (°Tw), Beaume (°Be), and Specific Gravity (S.G.)

°Tw	°Be	S.G.	°Be	°Tw
0	0·0	1·00	0	0·0
2	1·4	1·01	1	1·4
4	2·8	1·02	2	2·8
6	4·2	1·03	3	4·2
8	5·6	1·04	4	5·7
10	6·9	1·05	5	7·1
12	8·2	1·06	6	8·6
14	9·5	1·07	7	10·1
16	10·7	1·08	8	11·7
18	12·0	1·09	9	13·2
20	13·2	1·10	10	14·8

°Tw	°Be	S.G.
22	14·4	1·11
24	15·5	1·12
26	16·7	1·13
28	17·8	1·14
30	18·9	1·15
32	20·0	1·16
34	21·1	1·17
36	22·1	1·18
38	23·2	1·19
40	24·2	1·20
42	25·2	1·21
44	26·2	1·22
46	27·1	1·23
48	28·1	1·24
50	29·0	1·25
52	29·9	1·26
54	30·8	1·27
56	31·7	1·28
58	32·6	1·29
60	33·5	1·30

°Be	°Tw
11	16·4
12	18·0
13	19·7
14	21·4
15	23·1
16	24·8
17	26·6
18	28·3
19	30·2
20	32·0
21	33·9
22	35·8
23	37·7
24	39·7
25	41·7
26	43·7
27	45·8
28	47·9
29	50·0
30	52·2

NOTE

No. 1 Twaddel hydrometer is graduated from 0°Tw to 24°Tw.
No. 2 Twaddel hydrometer is graduated from 24°Tw to 48°Tw.
No. 3 Twaddel hydrometer is graduated from 48°Tw to 72°Tw.

DENSITY OF SODIUM SULPHIDE AND SODIUM HYDROSULPHIDE

The densities are given in Twaddel (°Tw) and Beaume (°Be). The concentrations of sodium sulphide and sodium hydrosulphide are given as percentages of the pure salt, weight/volume (w/v). This corresponds to the number of grammes of the pure salt dissolved in 100 ml of solution, or the number of pounds dissolved in 10 gallons of solution. The commercial sodium sulphide and sodium hydrosulphide are not 100 per cent pure. To make up a 12 per cent solution with 60 per cent commercial sodium sulphide would require 20 lb per 10 gallons, not 12 lb.

SODIUM SULPHIDE

Percentage of Pure Sodium Sulphide, w/v	°Tw	°Be
3·8	8	5·6
4·3	9	6·3
4·7	10	6·9
5·2	11	7·6
5·7	12	8·2
6·2	13	8·9
6·7	14	9·5
7·2	15	10·1
7·7	16	10·7
8·1	17	11·4
8·6	18	12·0
9·1	19	12·6
9·6	20	13·2
10·1	21	13·8

SODIUM HYDROSULPHIDE

Percentage of Pure Sodium Hydrosulphide, w/v	°Tw	°Be
4·0	5	3·5
4·8	6	4·2
5·6	7	4·9
6·4	8	5·6
7·2	9	6·3
8·0	10	6·9
8·8	11	7·6
9·6	12	8·2
10·5	13	8·9
11·3	14	9·5
12·1	15	10·1
12·9	16	10·7
13·7	17	11·4
14·5	18	12·0

Sodium Sulphide

Percentage of Pure Sodium Sulphide, w/v	°Tw	°Be
10·6	22	14·4
11·2	23	15·0
11·7	24	15·5
12·2	25	16·1
12·7	26	16·7
13·2	27	17·3
13·8	28	17·8
14·3	29	18·4
14·8	30	18·9
15·4	31	19·5
15·9	32	20·0
16·4	33	20·5
17·0	34	21·1
17·6	35	21·6

Sodium Hydrosulphide

Percentage of Pure Sodium Hydrosulphide, w/v	°Tw	°Be
15·3	19	12·6
16·2	20	13·2
17·0	21	13·8
17·8	22	14·4
18·6	23	15·0
19·4	24	15·5
20·2	25	16·1

DENSITY OF SALT SOLUTIONS

The densities are given in Salinometer (°Sal) and in Beaume (°Be). The concentration of salt is given as a percentage weight/weight (w/w) and as a percentage weight/volume (w/v). The first of these corresponds to the number of grammes dissolved in 100 grammes of pickle liquor, or to the number of pounds per 100 lb of pickle liquor. The second corresponds to the number of grammes per 100 ml, or the number of pounds per 10 gallons. The two figures are different because 1 gallon of brine or pickle liquor weighs more than 10 lb.

		Percentage of Salt	
°Sal	°Be	w/w	w/v
37	9·9	9·8	10·5
38	10·1	10·1	10·8
39	10·3	10·3	11·1
40	10·6	10·6	11·4
41	10·9	10·9	11·7
42	11·1	11·1	12·0
43	11·3	11·4	12·3
44	11·6	11·7	12·6
45	11·8	11·9	12·9
46	12·1	12·2	13·3
47	12·3	12·5	13·6
48	12·6	12·7	13·9
49	12·8	13·0	14·2
50	13·0	13·3	14·5
51	13·2	13·5	14·8
52	13·5	13·8	15·1
53	13·7	14·0	15·4
54	13·9	14·3	15·8
55	14·2	14·6	16·1
56	14·4	14·8	16·4
57	14·6	15·1	16·7
58	14·8	15·4	17·1
59	15·1	15·6	17·4
60	15·4	15·9	17·7

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